Faculty of Engineering and Science

Developing a Reinforced Portland Cement using Nano Materials for CO_2 Sequestrated Reservoirs

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This Thesis is presented for the Degree of

Doctor of Philosophy

of

Curtin University

November 2019

Declaration

To the best of my knowledge and belief, this thesis contains no material previously published by any other person except where due acknowledgment has been made.

This thesis contains no material which has been accepted for the award of any other degree or diploma in any university.

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Acknowledgement

It is my pleasure to acknowledge many people who made this thesis possible.

Firstly, I would like to thank the almighty God for all help and mercy that guided me throughout my life and brought me till the end of my PhD study. Without His blessings and strength given, I couldn't accomplish this research in the best possible way.

I am profoundly grateful to my Thesis committees: chairperson - Associate Professor (AP) Dr Hisham Khaled, main supervisor - AP Dr Raoof Gholami, co-supervisor - AP Dr. Muhammad Rahman and associate supervisor - AP Dr Sonny Irawan. Particularly, I would like to thank AP Dr. Raoof Gholami for his unconditionally assistances, supports and mentorship. His valuable advices, motivation, guidance and patience have always inspired me to keep my determination and faith to strive to the very end of this PhD study.

At the same time, I wish to express my appreciation to the Faculty of Engineer of Curtin University, Malaysia for doing their best to fulfil my requests in order to get my experimental studies done. Particularly, I would like to thank the lab manager, Miss Helda as well as the lab technicians, Miss Diana, Miss Michelle, Mr. Mohd Hidayat, Mr Michael Ding, Miss Sharinna, Mr. Martin and Miss Beatrice for their assistances in the preparation of experimental works. They were always making themselves available to help when there was a machine breakdown or any lab related issues taking place. Besides, my heartfelt thanks to my supportive HDR friends, specifically Khizar Abid, who is very generous and helpful in providing me guidance whenever I face any problem in conducting the lab sessions.

Also, I am indebted to my lovely parents and siblings for their emotional support and endless encouragement. Without these, I would not have been possible to achieve whatever I have today.

Last but not the least, I sincerely acknowledge the financial support from the Ministry of Higher Education (MOHE) Malaysia under the Fundamental Research Grant Scheme (FRGS) FRGS/1/2015/TK05/CURTIN/03/4.

Publications

Journal papers:

1. Tiong, M., Gholami, R., Abid, K. 2019. Nanomodification: An Approach to Improve Cement Efficiency in CO2 Storage Sites. (ongoing review)

2. Tiong, M., Gholami, R., Rahman, M.E., 2019. "Cement degradation in CO_2 storage sites: a review on potential applications of nanomaterials." (Journal of Petroleum Exploration and Production Technology) 9(1): 329-340.

3. Abid, K., Gholami, R., Tiong, M., Nagaratnam, B., Sarmadivaleh, M., Mostofi, M., Bing, Chua, H.B., and Muktadir, G., 2019. "A pozzolanic supplementary material to reinforce class G cement used for drilling and completion operations." (Journal of Petroleum Science and Engineering) 177: 79-92.

Conference presentation:

1. Tiong, M., Gholami, R., Rahman M.E., and Irawan, S. An approach to enhance the durability and mechanical properties of Class G cement using nano materials, 11th Curtin University Technology, Science and Engineering International Conference (CUTSE), Miri, 26th – 28th November 2018. IOP Conference Series: Materials Science and Engineering, Volume 495, Number 1.

2. Tiong, M. Assessment of thermal, viscoelastic and mechanical properties of Nano Glass Flakes-Cement Nanocomposites: Role of Nano Glass Flake and Mixing Methods. One Curtin International Postgraduate Conference (OCPC), Miri, 26th – 28th November 2018.

3. Tiong, M. Enhancing Wellbore Integrity in CO_2 Sequestrated Reservoirs by Developing a New Class of Cement, 5th Postgraduate Borneo Research Colloquium 2017, Kuching, 4th - 6th July 2017.

4. Tiong, M., Gholami, R., and Rahman M.E. A Nanomodification Approach to Improve Cement Integrity in CO_2 Storage Sites, One Curtin International Postgraduate Conference, Miri, 10th – 12th December 2017.

Abstract

Global warming is one of the crucial problems that has received significant attention in the past decades. This temperature rise is linked to the release of greenhouse gases, particularly CO_2, into the atmosphere. To resolve or at least mitigate this problem, Carbon Capture and Storage (CCS) technology has been introduced as one of the most effective strategies to store CO_2 into subsurface layers and prevent it from being released into the atmosphere. However, it is challenging for CO_2 to remain confined under high-pressure high-temperature (HPHT) conditions of subsurface layers given the degradation of Portland cement induced by the chemical interaction with wet/dry CO_2. Several studies have been done to improve the cement resistance against the attack of CO_2 but limited success has been reported to the application of these methods once tested under different conditions. Thus, in this study, attempts were made to develop a methodology using nanomaterials which can improve the performance of the cement once exposed to CO_2. Given the salient feature of nanomaterials such as large surface areas, fast interaction and heat resistance, Nano Glass Flake (NGF) and Multiwall Carbon Nano Tube (MWCNT) were considered as good supplementary materials to improve cement efficiency.

A series of precarbonation and postcarbonation tests, including rheology, compressive strength, thermogravimetric analysis (TGA) and X-ray diffraction (XRD) were conducted on the cement samples modified by NGFs and MWCNTs. The results obtained from the precarbonation tests indicated that the density of NGFs based cement remained the same as that of the neat cement whilst the plastic viscosity becomes higher. It was also recommended to not to add more than 1 wt.% NGFs to the cement due to the creation of a high viscosity paste that may negatively impact on the pumping operation. This threshold for the viscosity of MWCNTs, on the other hand, was around 0.25 wt.%. The result obtained showed that the cement with small amount (0.05 wt.%) of MWCNTs could show a huge compressive strength after 28 days of curing. The sonicated mixing approach proposed for the sample preparation appeared to have a positive impact on the physical and mechanical properties of the

cement. It was concluded that by adding nanomaterials and applying a good dispersion method, not only the overall physical performance of the cement can be improved, but also a lesser amount of portlandite would be produced which is very crucial to have a better resistance against the attack of CO_2.

Those samples with the best performance from different categories in the precarbonation stage were exposed to water-saturated supercritical $scCO_2$ in a static reactor for 56 days. A series of tests were then conducted on the samples in the postcarbonation stage where it was observed that CO_2 diffuses into the cement and promotes cement disintegration. Increasing the weight of the samples indicated that the cement was carbonated while the cement samples with 0.5 wt.% NGFs and 0.05 wt.% MWCNTs had the smallest carbonated areas. However, different samples had different degree of carbonation due to the quantity of nanoparticles added. It was revealed that MWCNTs gives a better performance to the cement in terms of compressive strength, as they are able to control the morphology of $CaCO_3$ crystals. Nevertheless, NGFs based cement could be a better option in terms of resistance against the attack of CO_2 because it had a lesser amount of portlandite in its structure, which is a highly reactive component toward CO_2. This would lead to the leaching and reduction of the cement durability. In addition, given the fact that NGFs are significantly cheaper than MWCNTs, they can be a very great asset to improve the cement performance in the CCS operation without posing significant cost on the projects.

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Nomenclature

α	radius of the particles (cm)
ε	dielectric constant
$f(k\alpha)$	Henry function
K	consistency index (Pa s^n)
k	thickness of the electrical layer
m_s	mass of cement slurry (g)
η	zero-shear velocity
n	power law exponent
P	pressure (MPa)
p	density/specific gravity (g/cm^3)
T	temperature (°C)
t	time (s)
μ	viscosity (cp)
V_{ff}	volume of the free fluid (ml)
Z	zeta potential
$\%_{ff}$	percentage of free fluid (%)

List of Abbreviations

ASR	alkali-silica reaction
CNTs	carbon nanotube
CSS	carbon capture and storage/sequestration
ECR	electrical and chemical resistant
EOR	enhanced oil recovery
GF	glass powder
H	manual/hand mixing
HPHT	high pressure high temperature
IEA	International Energy Agency
MIP	mercury intrusion porosimetry
MW	molecular weight
MWCNTs	multiple-walled carbon nanotubes
NC	neat cement
NGFs	nano glass flakes
NS	nano silica
$scCO_2$	supercritical carbon dioxide
PCBs	polychlorinated biphenyls
RHA	rice husk ash
S	ultrasonication
SWCNTs	single-walled carbon nanotubes
SDS	sodium dodecyl sulfate
TEM	transmission electron microscopy
TGA	thermogravimetric analysis
UCA	ultrasonic cement analyzer
UTM	universal testing machine
w/c	water to cement ratio
WGP	waste glass powder
WOC	waiting on cement
XRD	X-Ray diffraction analysis
ZS	zetasizer

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Chapter 1: Introduction and Fundamentals

1.1. Introduction

Carbon Capture and Storage/Sequestration (CCS) technology has been employed worldwide to reduce the amount of greenhouse gases, especially carbon dioxide (CO_2), released into the atmosphere. This is mainly because CCS appears to be an effective mechanism by which a large amount of CO_2 can be stored into subsurface layers such as depleted hydrocarbon reservoirs, saline aquifers and coal beds for thousands of years (Gaurina-Medimurec, et al., 2010, Takase et al., 2010).

The concept of CCS was introduced in 1977 when CO_2, which was emitted from a coal power plant, was captured and injected into a geological formation (Marchetti, 1977). This technology has been widely accepted since the successful injection and storage of CO_2 into an aquifer located 800 meters beneath the North Sea 30 years ago (Benson and Cole, 2008). Canada and Algeria followed the footsteps ever since and started their CCS projects by injecting 20 million tons (Mt) of CO_2 into their depleted hydrocarbon reservoirs (Benson and Cole, 2008; Takase et al., 2010). According to the modelling done by International Energy Agency (IEA), by 2050, about 19% of total greenhouse gas emission can be reduced, using CCS technology (Claussen, 2012).

Depleted reservoirs are often chosen for CO_2 storage due to their geological history, integrity and infrastructures. The abundant and closed wells of these reservoirs can be used as the conduits to inject CO_2 where conventional class G cement is employed to seal off the injection intervals. However, class G cement is composed of Portlandite and in an aqueous medium, can react with CO_2, resulting in significant cement sheath degradation. As a result, leakage paths are induced in the cement, causing seepage of CO_2 and environmental contaminations (Xu et al., 2007; Bachu and Bennion, 2009; Zhang et al., 2013; Ansarizadeh, et al., 2015, Bruno et al, 2019). Therefore, it is essential to understand the chemical composition and kinetic reactions of the cement and components susceptible to CO_2 attack before implementing a CCS project. It is also crucial to discuss the possible effects of

carbonation/bicarbonation on the mechanical and transfer properties of the cement to ensure the long-term integrity of wells and the storage sites.

1.2. CO_2 Sequestration

1.2.1. Deep Geological Formations

Storage sites are often depleted oil and gas formations and brine aquifers with the capacity of handling 675 to 900 billion tons of CO_2 (IPCC, 2005; Benson and Cole, 2008). Usually, oil and gas industry would inject CO_2 into particular deep (more than 800m deep) geological formations (reservoirs) to improve the production, in a process known as Enhanced Oil Recovery (EOR). Once these reservoirs are completely depleted and verified as a safe geological storage site, the CCS technology can be considered for the storage purposes (Benson and Cole, 2008; Gaurina-Medimurec, et al., 2010).

Once injected into the storage sites, CO_2 must be monitored carefully as it has different physical properties at different temperature (T) and pressure (P) conditions. For instance, at the ambient temperature, CO_2 appears as a gas but it becomes a supercritical fluid under the temperature of 32°C and the pressure of 7MPa (Oldenburg, 2007; Sauki and Irawan, 2010), which often happen at a depth of greater than 800m. Figure 1.1 shows the CO_2 phase diagram under different temperature and pressure conditions.

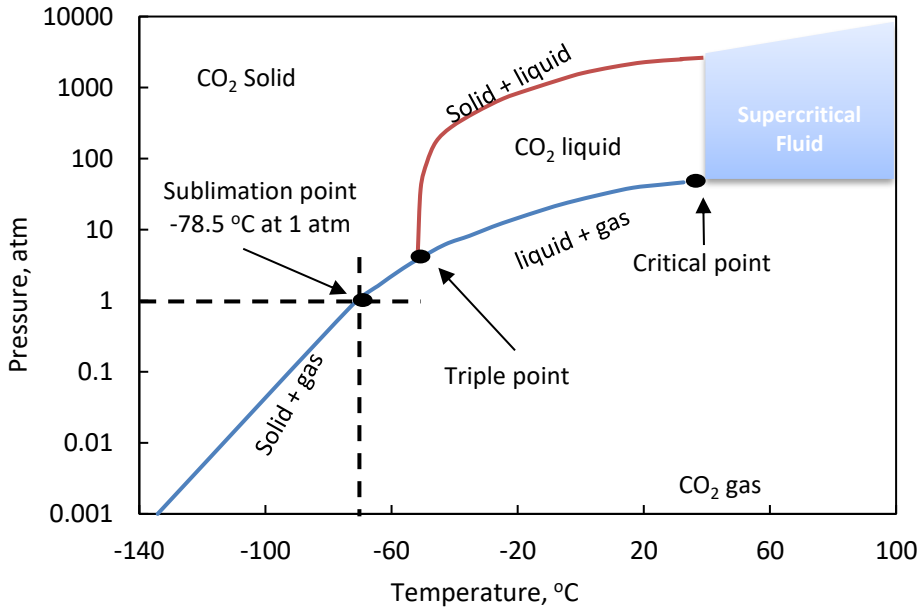


Figure 1.1: CO_2 phase diagram (modified after Oldeburg, 2007)

1.2.2. Cement Systems

Secondary cementing such as filling the voids or sealing off the injection intervals must be done upon injection to prevent CO_2 seepage back to the surface or any other valuable resources. As a result, a good cementing material with a good physical characteristic must be chosen to reduce the risk of leakage.

A good well cement should have an adequate pumping time, appropriate rheology, low water loss and no free water bleeding (Lesti et al., 2013). There are eight classes of cement listed in the API standard for oil well cementing which are categorized based on their specifications and functionality, among which Class G (Portland) cement is the most common choices. This class of the cement typically consist of four main components including Tricalcium Silicate (C_3S), Dicalcium Silicate (C_2S), Tricalcium Aluminate (C_3A) and Tetracalcium Aluminoferrite (C_3AF) which give specific functionality to the cement as reported by Table 1.1.

Table 1.1: Major components of Portland cement (modified after Adams and Charrier, 1985)

Compound	Chemical Composition	Cement Chemist Notation	Concentration (wt %)	Purpose
Tricalcium Silicate	$(CaO)_3$. SiO_2	C_3S	55-65	Enhances the strength and develops early strength.
Dicalcium Silicate	$(CaO)_2$. SiO_2	C_2S	15-25	Hydrates slowly, strength generated over an extended period of time.
Tricalcium Aluminate	$(CaO)_3$. Al_2O_3	C_3A	8-14	Promotes rapid hydration, affects thickening time and initial setting of the cement and makes the cement vulnerable to sulphate attack.
Tetracalcium Aluminoferrite	$(CaO)_4$. Al_2O_3. Fe_2O_3	C_3AF	8-12	Responsible for slow hydration.

C_3S is the most abundant component of the cement which hydrates faster than the other three (Nelson, 1990). When water is mixed with the cement, hydration takes place. Wang (2017) claimed that most of the reactions are exothermic and the main reactions of hydration occur within the first 24 hours, although the hydration will continue until the full consumption of the reactants (>1 year). The hydration process is usually divided into four major periods under these circumstances: i) initial reaction and rapid heat generation (last for a few minutes), ii) slow reactions, iii) acceleration period and iv) deceleration period (Bullard et al., 2011). Acceleration period is considered as one of the most important periods by which a huge amount of hydrates is produced. It is mainly because of the silicate reaction as explained by the equations below (MacLaren and White, 2003; Omosebi, et al., 2016):

$$2C_3S + 6H_2O \rightarrow C_3S_2H_3 + 3Ca(OH)_2 \quad (1.1)$$

$$2C_2S + 4H_2O \rightarrow C_3S_2H_3 + Ca(OH)_2 \quad (1.2)$$

Calcium Silicate Hydrate (C-S-H) is the major component produced upon the cement hydration together with calcium hydroxide ($Ca(OH)_2$). In the cement paste, calcium silicate creates a strong connection between the cement grains, leading to the development of the cement strength while $Ca(OH)_2$ basically act as the binder.

1.3. Portland Cement Degradation: Carbonation and Bicarbonation

To understand the chemical reactions taking place between CO_2 and Portland cement, Kutchko et al. (2007) carried out an experimental study to simulate a real reservoir condition. They concluded that the cement degradation is linked to three main processes including i) C-S-H structural transformation, ii) carbonation of portlandite or calcium hydrate (CH or $Ca(OH)_2$), and iii) leaching of calcium carbonate ($CaCO_3$). The interactions and mechanisms included in the cement degradation are shown schematically in Figure 1.2.

Once injected into a storage site, CO_2 dissolves into the brine, which often exists in a reservoir after hydrocarbon production. As a result, carbonic acid (H_2CO_3) is produced (Eq. (1.3)) which reduces the pH of the aqueous environment significantly.

$$CO_2\,(aq) + H_2O \rightarrow H_2CO_3\,(aq) \quad (1.3)$$

As the acid diffuses into the hydrated cement, Portlandite is attacked (expressed by Eq. (1.4)), with a faster rate than C-S-H due to its higher reactivity (Omosebi, et al., 2016). This interaction brings down the pH of the solution even further.

$$Ca(OH)_2\,(s) \rightarrow Ca^{2+}\,(aq) + 2OH^-\,(aq) \quad (1.4)$$

Due to the depletion of Portlandite and leaching of Ca^{2+} out of the cement matrix, the porosity of the cement increases and precipitation of calcium carbonate ($CaCO_3$) takes place as addressed by Eq. (1.5). Under these circumstances, $CaCO_3$ acts as a filler and occupies the pore space of the cement. In fact, production of $CaCO_3$ not only reduces the porosity and permeability by the densification of the cementitious matrix, but also increases the compressive strength. This process, known as carbonation, is thermodynamically favoured and cannot be avoided (Santra and Sweatman, 2012).

$$Ca^{2+}(aq) + HCO^{3-}(aq) + OH^-(aq) \rightarrow CaCO_3(s) + H_2O \quad (1.5)$$

Although the carbonation improves the cement resistance against the CO_2 attack, crystallization of $CaCO_3$ would lead to the volume expansion and cracking. This would offer a route for CO_2 migration through the cement matrix.

Once portlandite is completely consumed, $CaCO_3$ starts to dissolve due to its continuous reaction with carbonic acid, which leads to leaching of Ca^{2+} and domination of HCO^{3-} as expressed by Eq. (1.6). Dissolution of $CaCO_3$, on these occasions, is called bicarbonation. Calcium bicarbonate is soluble in water and would easily disperse out of the cement matrix.

$$H+\,(aq) + CaCO_3\,(s) \rightarrow Ca^{2+}\,(aq) + HCO^{3-}\,(aq) \quad (1.6)$$

As a result, the remaining C-S-H is converted into an amorphous silica gel ($amSiO_2$) (See Eq. (1.7)). Eventually, the amount of Ca^{2+} gradually increases and more pores are created within the cement matrix which leads to the loss of zonal isolation and migration of CO_2 to surface/subsurface resources (Kutchko, et al., 2007; Zhang and Talman, 2014).

$$C\text{-}S\text{-}H\,(s) \rightarrow Ca^{2+}\,(aq) + OH^-\,(aq) + amSiO_2\,(s) \quad (1.7)$$

Zhang and et al., (2014) claimed that three distinct regions are generated as the carbonation progresses including: i) uncarbonated zone, ii) transition zone (a region with a high porosity), and iii) carbonation zone.

Usually, white particles are observed in the uncarbonated cement indicating that the neat cement is not completely hydrated. In the transition zone, porosity increases due to the dissolution of hydration phases. Presence of partial decomposition of unhydrated cement confirms this process. In the carbonated zone, on the other hand, precipitation of calcium carbonate occurs. Thus, a carbonated neat cement would have two distinct features: i) leaching of calcium carbonate near the surface and ii) overgrowth of the calcium carbonate near the surface. When the cement is carbonated for a long time, calcium carbonate crystals would overgrowth further on the surface (Zhang et al. 2014).

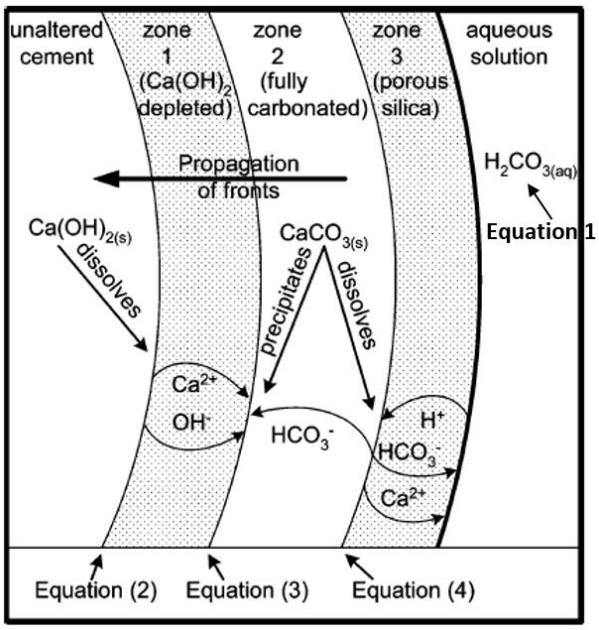


Figure 1.2: Interactions taking place in the cement once exposed to CO_2 (Kutchko et al, 2007)

1.4. Research Contribution Statement

The project contributes towards the advancement of well cementing by developing a reinforced cement using nanomaterials that can withstand the harsh environment of CO_2 storage site. The cement developed as part of this study could be used for the secondary operations given its huge strength and corrosion resistance characteristics. Through the development of this nanomaterial-based approach and studying its feasibility in the cement industry, this research can save the operation cost and maintain the well integrity, specifically in CO_2 sequestrated reservoirs.

1.5. Research Significance

Geological sequestration of greenhouse gases has been the subject of interest in the past decades, where concerns about the safety and security of storage sites have been raised. The issue of the cement degradation under the acidic environment of a storage site has been one of these concerns which have not been totally resolved/understood. This study attempts to provide a deeper insight into the process of the cement disintegration in the CCS sites and propose a nanomodification approach which can enhance the cement sheath integrity during and after CO_2 injection.

1.6. Research Objectives

This research aims to enhance the cement resistance against the attack of CO_2 using nanoparticles which is also known as nanomodification. It is the major methodology taken and two nanoparticles known as nano glass flakes (NGFs) and multiple-walled carbon nanotubes (MWCNTs) were considered. In particular, this project attempts to achieve the following objectives:

I. Characterization of the cement before and after nanomodification.
II. Determination of nanomaterials quantity required to give the best performance to the cement once exposed to a CO_2 rich environment.
III. Proposing an appropriate dispersion method which can create a perfect bond between the cement structure and nanomaterials used.
IV. Reinforcing the Portland cement using MWCNTs and NGFs which can withstand the acidic environment of a storage site, mainly consists of supercritical CO_2.

1.7. Research Questions

Based on the research objectives, the following questions must be answered.

I. How nanomodification can change the physical and mechanical properties of the cement?
II. What would be the quantity of CNTs and NGFs required to create a suitable cement for a CO_2 storage site?

III. What is the best approach to disperse nanomaterials into the cement matrix and reduce/prevent cement degradation under supercritical CO_2 conditions?

IV. Which one of the nanoparticles (CNTs and NGFs) used is a better choice for the cement reinforcement?

1.8. Scope of Study

This research is focused on the well cementing operation especially for CO_2 sequestration sites where cement integrity is a concern. In this regard, the Interactions between CO_2 and well cement will be deeply studied and a proper stepwise guideline will be provided as to analyse the cement before and after exposure to CO_2. The improvement made by nanomaterials on the well cement will be the main discussion as it is the approach taken to reinforce the cement against the attack of CO_2.

1.9. Thesis Organization

This thesis provides a guideline as to how nanoparticles can be employed to enhance the cement resistance against the attack of CO_2. Chapter 1 delivers a background study on the CO_2 sequestration and the interaction taking place between the cement and CO_2. After this chapter, Chapter 2 provides a good summary of previous studies performed on the cement degradation in CO_2 storage sites. Over there, the approaches proposed so far for the cement reinforcement are discussed and the application of nanomaterials such as NGFs and MWCNTs are discussed. This is followed by Chapter 3 and 4 where the application of NGFs and MWCNTs in the primary cementing stage is examined. The methodology of mixing nanoparticles with the cement is explained in these chapters and the differences between the cement properties before and after the nanomodification are presented. Chapter 5 focuses on the carbonation of the neat and nanomodified cement composites where the process of carbonations and the rate of degradation in different cement samples are thoroughly examined and discussed. Analytical studies are also presented to understand how the carbonation changes the cement performance. Last but not least, chapter 6 gives a summary of findings and provides some discussions and conclusions.

Chapter 2: Literature Review

2.1. Introduction

As it was mentioned in the first chapter, cement degradation induced by exposure to CO_2 is the main concern of this study. Thus, in this chapter, attempts are made to provide a comprehensive review on different aspects of the cement sheath integrity in CO_2 storage sites. A good discussion on the latest methods of nanomodifications developed so far for the cement reinforcement is also provided followed by a conclusion on the most promising nanomaterials that can improve the cement performance under downhole conditions.

2.2. Neat Cement Degradation

2.2.1. Experimental studies on the neat cement degradation

Many experimental studies have been carried out to evaluate cement degradation under HPHT condition to simulate reservoir conditions. These studies are categorized into two classes where: 1) cement is exposed to $scCO_2$ saturated brine (wet) and 2) cement samples are solely tested against $scCO_2$ (dry) (Kutchko, et al., 2007, 2008; Barlet-Gouedard et al., 2009; Sauki and Irawan, 2010; Duguid and Scherer, 2010; Laudet, et al., 2011). For instance, Barlet-Gouedard et al. (2007) suggested that brine should be used for the carbonation test rather than freshwater. They used a 0.4M NaCl brine solution and observed a dramatic fall in the propagation rate of the cement samples after two days of exposure to CO_2 saturated brine. Propagation fronts of CO_2 were studied and three distinct zones were distinguished in the cement samples. To examine the effect of temperature and pressure on the cement degradation, Irawan and Arina (2010) conducted an experiment by preparing the neat Class G cement according to the API recommended practices. They cured the cement for 8 hours at different temperatures (i.e., 40^{o}C and 120^{o}C) and pressures (i.e., 10.5 MPa and 14.0 MPa). It was concluded that HPHT conditions reduce the compressive strength, causing densification of C-S-H, which would increase the rate

of degradation. Barlet-Gouedard et al. (2009) found out that the degradation of the cement is faster under high temperature (90^{o}C) and high pressure (20.68 MPa) condition.

Laudet et al. (2011) carried out a carbonation test on the neat Class G cement for 90 days at the pressure of 8MPa and two different temperatures of 90^{o}C and 140^{o}C. A faster carbonation front was observed at 140^{o}C due to the mineralogical nature of hydrates which reduces the cement transport properties and ultimately limits the carbonation process. They emphasised that wellbore temperature and pressure should be monitored carefully before the cement formulation.

To further understand the behaviour of Portland cement under CO_2 rich environments, Kutchko, et al. (2007 & 2008) carried out a series of experiments where neat class H cement samples were exposed to $scCO_2$ under the reservoir condition (i.e., the pressure of 30.3 MPa and the temperature of 50^{o}C). Kutchko, et al. (2007) observed that the cement resistance depends mainly on the curing environment. In fact, the cement cured under the HPHT conditions for 28 days had the least amount of CO_2 penetration due to the formation of calcite. This study was further investigated by Kutchko et al. (2008) in which the period of carbonation test was extended from 9 days to 1 year. The results obtained indicated that the carbonation reaction is a diffusion-controlled phenomenon for samples exposed to $scCO_2$. Duguid and Scherer (2010) did a series of experiments to study the relationship between cement degradation and pH variation. There was no degradation in the samples exposed to $scCO_2$ having a leaching solution of pH 5. Hence, they concluded that if $CaCO_3$ can be dissolved into the formation water, as long as pH increases, the degradation may stop. This could be the reason why sandstone reservoirs have a greater carbonation front compared to carbonate reservoirs as they do not have $CaCO_3$ to be dissolved into the formation water. However, this experiment was conducted under the dynamic condition and may not be a true representative of the reservoir conditions. The dynamic condition here is referred to as the situation where CO_2 flows through the reactor and goes in and out while there is no flow rate in the static condition. It also should be noted that under the dynamic condition, the cement carbonation rate would be accelerated (Kutchko, et al., 2007).

2.2.2. Developed Approaches to Improve Cement Resistance

As it was mentioned earlier, the carbonation of Portland cement is inevitable. As such, a number of methodologies were proposed to enhance the cement resistance against the attack of $scCO_2$ as summarised in Table 2.1.

Table 2.1: Approaches developed to improve the cement resistance (Abid et al., 2015)

Approaches	Results
Pozzolanic material	• Reducing the permeability and quantity of the portlandite. As permeability decreases, the ingression of CO^{3-} and carbonation slows down (Brandl et al., 2010; Bai et al., 2015). • Reducing the water content in the cement creates a longer chain of C-S-H, which increases the strength of the cement. • An excessive amount of pozzolanic materials may result in a poor strength development (Brandl et al., 2010; Zhang et al., 2014). • Rheology of the pozzolanic cement increases over time. This would have a negative impact on the dispersion process and make it almost unlikely to take place (Vakili et al., 2013).
Decreasing Water/cement ratio	• Increasing the unhydrated cement clinker which eventually decreases the permeability. • Increasing the density may increase the fracture possibilities. • May result in creating fractures in heavy weight cement (Barlet-Gouedard et al., 2012).
Non-Portland cement (NPC)	• It is not sufficient for long-term integrity and not generally recommended because of its accessibility (Benge, 2009). • The hydration products are resistant to CO_2 (Takase et al., 2010). • NPC has a low environmental impact and does not require additional energy for material production (Jiang et al., 2014). • However, NPC loses more moisture and exhibits larger shrinkage compared to Portland cement (Ye & RadliNska, 2016).
Special additives	• Latex - Improves the bonding strength and controls the filtration loss. It allows a good strength development. The resistance against

	CO_2 attack will, however, not be significantly improved due to a low quantity of $CaCO_3$ (Bai et al., 2015). - In the presence of H_2SO_4 and Na_2SO_4, natural rubber latex enhances the impermeability and water exclusion properties of normal concrete. However, the compressive strength of the latex modified concrete decreases with increasing temperature (Bala & Ismail et al. 2012). • Epoxy resins - Will chemically coat the cement but it was degraded when tested at 90ºC and 28 MPa for 31 days (Barlet-Gouedard et al., 2012). - Incorporation of resins in the cement-based materials would improve the workability (fast setting) and durability (Wang, 2006; Vijayan et al., 2017). - However, it is much costly than cement, needs complex mixing methods and may have flammable properties (Pang et al., 2018).
Nano Materials	• Nano silica improves the microstructure and the strength of the cement by decreasing the porosity and permeability (Choolaei, et al, 2012). • clay nanocomposites increase tensile strength (Chang et al., 2007). • Nano-iron enhances the compressive strength (Hui et al., 2004). • However, a good dispersion technique must be used to improve their performance once added to the cement.

Looking into the approaches presented in Table 2.1, it appears that the overall performance of the cement can be enhanced if the supplementary materials/suggested approaches were properly selected and used. However, the enhancement achieved by nanomaterials seems remarkable, mainly because of their large surface area, fast interactions and better capability to cope with the HPHT condition.

2.3. Current Cement Nanomodification

Cement is composed mainly of different nano/micro size crystals and amorphous calcium-silicate-hydrate (C-S-H). As mentioned earlier, C-S-H acts as the binder of the cement, which is one of the key components governing the cement's durability. Hence, the nano-sized C-S-H particles with an average size of 5-10 nm can significantly reduce the porosity and permeability of the cement (Sobolev, 2015). As a matter of fact, cement nanomodification could be an effective approach to improve the cement strength and integrity under different downhole conditions (Lee, 2012). It should be noted that nano atoms can be easily attached to the surface of each particle and increase the surface area to volume ratio, which potentially increases the mechanical strength and reduces porosity. Moreover, adding nanoparticles promotes the hydration process at the early stages, due to the large surface area of particles (Zhang and Li, 2011; Choolaei et al., 2012; Meng et al., 2012). Sanchez and Sobolev (2010) highlighted the following advantageous of adding nanoparticles to the cement:

- Well-dispersed nano-particles can help to suspend the cement grains by increasing the viscosity of the liquid phase. At the same time, they can improve the segregation resistance and workability of the system;
- Nano-particles fill the voids between the cement grains, ceasing the movement of "free" water;
- Well-dispersed nano-particles can accelerate the hydration by acting as the centre of crystallization for the cement hydrates;
- Nano-particles favour the formation of small-sized crystals and small-sized uniform clusters of C-S-H;
- Nanoparticles enhance the structure of the aggregates' contact zone, resulting in a better bond between aggregates and the cement paste;
- Nanoparticles can provide crack arrest and interlocking effects between the slip planes, which improves the toughness, shear, tensile, and flexural strength of the cement-based materials.
- Tremendous surface area/volume ratio of nanomaterials alters the chemical reactions of hydrating cement and enhances the mechanical strength.

Recent studies have shown that the presence of nanoparticles can improve the physical and mechanical characteristics of the Portland cement. Many of these studies, reviewed in the next section, are borrowed from the civil industry due to the limited number of research works carried out in the areas linked to oil well cementing. However, since a very same type of the cement used, the discussion provided would be applicable to the oil well cementing.

2.3.1. Nano-silica (Nano-SiO_2)

Nanosilica has been used in many studies to improve cement integrity since it is the cheapest nano-particle oxide (Ershadi et al., 2011; Choolaei et al., 2012). Qing et al. (2007) found that nanosilica, in a low dosage (3% wt), can reduce the amount of calcium hydrate (portlandite), and as such improves the compressive and bonding strength at the early stage of hardening. Ershadi et al. (2011) conducted an experiment by adding nanosilica to the class G cement. The water to cement ratio of 0.6 was used to produce cement slurry with a large thickening time, high porosity and low compressive strength. They indicated that adding nanosilica improves the rheological and mechanical properties of the cement while the porosity and permeability decrease by 33% and 99% respectively. This could be due to the filler characteristics of nanosilica, which can enhance the microstructure and promote further pozzolanic reactions (Ershadi et al., 2011; Choolaei et al., 2012).

The study of Said et al. (2012) confirmed the filler and pozzolanic effects of nano-silica on the cementitious matrix. They obtained positive results from reactivity, strength development and refinement of pore structure. For instance, the addition of nano-silica could speed up the kinetics of hydration reactions and increase the compressive strength at all curing ages. Not to mention, mercury intrusion porosimetry (MIP) results showed that the total porosity and the threshold pore diameter were much lower for the cement samples with nanosilica.

Choolaei et al. (2012) emphasized on the great increase of the compressive strength after adding nanosilica to an ordinary Portland cement. They also indicated that the porosity and permeability of the cement decrease once an optimum quantity of nanosilica used. They concluded that a certain quantity of nanosilica must be added to the cement for the best functionality. A very similar conclusion was made by

Mendes et al. (2014). They highlighted that a large amount of nanosilica would reduce the performance of the cement while a small amount would not make any significant changes. However, the observation made by Ghafoori et al. (2016) was not aligned with the earlier studies. They replaced Portland cements (Class I) with 6 wt. % nanosilica and fully submerged the samples into a 5% chemical sodium sulfate (Na_2SO_4) solution for 1 year. Their mercury intrusion porosimetry (MIP) test showed a higher volume of pores in the macropores range in nanosilica mixture. This could be due to the agglomeration of nanosilica during mixing and lack of a proper dispersion method. They highlighted that agglomeration of nanosilica ceases the generation of nucleation sites inside the cement matrix and as such the density of the cement paste increases.

To test the flowability and consistency of the cement paste, Zabihi and Ozkul (2018) used a flow table test device described in ASTM Standard of C 230/C 230M for the cement mixture with a small dosage of nanosilica. It was found that a small amount of nanosilica, would have a negative impact on the flowability. When 0.5% of cement was replaced by nanosilica (15 nm average particle size), the flowability decreased by almost 40% due to the increase in the total surface area. Hence, they suggest a superplasticizer to decrease the water demand. This was the same conclusion drawn earlier by Quercia et al. (2012) where they found out that as the content of nanosilica increases, the workability decreases.

Regarding the resistance against the carbonation, nanosilica appeared to be a promising supplementary cementitious material due to its pozzolanic reaction which induces secondary chemical reactions and form additional C-S-H. This would reduce the permeability and accelerate the early strength devolvement (Jeong et al., 2018; Li et al., 2019; Xu et al., 2019; Wan et al., 2019).

Wan et al. (2019) mixed 0.5 and 1 wt.% nanosilica with portlandite cement and exposed to CO_2. At the w/c ratio of 0.45, 1 wt.% nano-silica gave the best results and could decrease the carbonation depth by 45.7% after 28 days. Jeong et al. (2018) looked into the curing conditions and replaced 2% of nano-silica with the Portland cement. They cured the samples for 28 days under different temperature and pressure conditions. It was then revealed that the degradation zone exhibited by the samples with nanosilica is approximately 20% lesser than those without nanosilica.

According to them, regardless of the curing conditions, nanosilica can fill up the existing pores and reduces the penetration rate of CO_2 into the cement matrix. However, curing at high pressure and temperature condition can accelerate the hydration and improve the strength, due to the formation of C-S-H silicate polymerization. Li et al. (2019) examined the effect of nanosilica on the long-term carbonation resistance of the concrete treated with polymer coatings, such as chlorinated rubber, epoxy resin, and polyurethane. They revealed that with a suitable dosage of nanosilica, the carbonation resistance improves by 44% and the polymers service life increases by 78%. Hence, with an optimum quantity of nanoparticles and a good curing condition, improvement of the cement performance under downhole conditions, especially in CCS sites, is anticipated.

2.3.2. Nano-iron (nano-Fe_2O_3)

Nanoscale iron particles have been widely used in medical and laboratory applications, as well as cost-effective remediation of industrial sites, treating several forms of ground contamination, such as polychlorinated biphenyls (PCBs), chlorinated organic solvents, and organochlorine pesticides. Due to its large surface area, it is considered as a very reactive and easy to transport materials, which is favourable to do in-situ treatments. They can be catalysed to further enhance the speed and efficiency of remediation. However, these metallic nanoparticles tend to agglomerate on the soil surface during the remediation (Zhang, 2003).

Li et al. (2004) mixed 3-10% of nano-iron with Portland cement and cured the samples for 7 and 28 days. They discovered that the quantity of 3% gave the best result – increases the compressive strength by 25 % and the flexural strength by 18%. These results indicated that the optimal content of nano-iron to reinforce the concrete should be less than 10%. They also mixed the cement with nano-iron, together with nano-silica but the strength was lower than the mortar mixed with only one nanoparticle.

Amer et al. (2015) synthesized and mixed 1 - 3 wt.% nano-iron with the cement in order to test its durability against high temperature conditions. Generally, all nano-modified cements provided higher strength than the neat cement. They indicated that nano-iron can act as a filler and reduces the porosity. This nanoparticle can also

accelerate the CSH gel formation, increases the crystalline $Ca(OH)_2$ content and as such improves the strength.

Sanjuan et al. (2018) mixed their cements with 0–6 wt.% nano-silica and 0–4 wt.% nano-iron with the water to cement ratio of 0.5. After curing for 2, 7 and 28 days, they observed that the compressive strength of the nano-modified mortars is lower than those obtained with the control set. The greatest reduction was found in the cement with 4 wt.% nano-silica and 4 wt.% nano-iron respectively after 28 days. They assumed that applying two nanoparticles at the same time is not a good practice as they cannot be well dispersed. This could cause aggregating and create voids in the cement matrix. Consequently, a homogeneous hydrate microstructure cannot be formed, and a low strength will be expected. Other possible reasons leading to poor strength development could be the lack of water in the cement and unsuitable curing method.

2.3.3. Nano-alumina (nano-Al_2O_3)

Several studies have been carried out to investigate the application of nanoalumina in the cement and concrete industry. Oltulu and Şahin (2011) studied the single and combined effects of nano-powders (nanoalumina and nanosilica) on the cement strength and permeability. They added 0.5 wt%, 1.25 wt% and 2.5 wt% binder amount and the compressive strength was tested at the early (i.e., 3 and 7 days), standard (i.e., 28 days), and late stages (i.e., 56 and 180 days). The best result for both compressive and permeability was observed when 1.25 wt% nanoalumina was used. They concluded that nanoalumina is a better option than nanosilica when it comes to the improvements of the physical and mechanical properties of the cement. They also indicated that a combination of these two may lead to agglomeration, causing negative changes of the physical-mechanical properties of the mortar.

To study the relationship between the sulfate attack and cement nanocomposites (nano-alumina and nanosilica), Jahangir and Kazemi (2014) added 0.1 kg nanosilica and 0.05 kg nanoalumina into 1 kg cement and exposed the samples to a 10wt% sulfuric acid solution. They cured the samples at the room temperature for 24 hours. Tests were carried out after 3, 7 and 28 days. Their study indicated that the compressive strength increases by as much as 50% when a combination of nanosilica

and Nanoalumina is used. It was also found that the nanocomposites produced had lesser expansion compared to the neat cement.

Heikal et al. (2015) replaced cement with 1 wt%, 2 wt%, 4 wt% and 6 wt% nanoalumina to examine the cement strength development. Polycarboxylate based superplasticizer was used as part of this study to maintain the rheology of the cement slurry. Cement samples were cured for 28 days in a water bath and the results revealed that adding nanoalumina enhances the hydration of the cement by accelerating the setting times and can increase the compressive strength. They concluded that 1 wt% nanoalumina is the optimum amount to improve the physical and mechanical properties of the cement.

Shao et al. (2019) and Zhou et al. (2019) carried out experimental studies on blending 5% nano-alumina with Portland cement at a 0.5 w/c ratio and found out that the nano-alumina not only acts as a filler and improves the strength but also poses chemical interactions that can increase the pozzolanic impact on the long-term strength development. Both studies revealed that adding nano-alumina would lead to the formation of additional Al-bearing phases, such as ettringite and monosulfate, which can increase the consumption of portlandite and improve the bound water content. According to Shao et al. (2019), addition of nano-alumina increases the compressive strength and reduces the porosity. The greatest difference of the compressive strength was observed in the samples cured for 180 days.

Zhou et al. (2019) dispersed nano-alumina in the cement paste using ultrasonication for 10 min. They claimed that the continuous dissolution of nano-alumina would lead to the formation of additional ettringite in the cement matrix. This formation can be the source of promoting the depletion of gypsum, which accelerate the reaction of aluminate (C_3A). This can decrease the porosity, refine the pore structure, and enhance the strength.

2.3.4. Nano-titanium dioxide (nano-TiO_2)

Nanotitanium dioxide has been used in several studies to improve the cement integrity given its photocatalytic properties (Lee and Kurtis, 2010; Chen et al., 2012). Unlike nanosilica, nanotitanium oxide is a non-reactive filler and does not pose any pozzolanic activities (Chen et al., 2012). Zhang and Li (2011) conducted a test on the

concrete and demonstrated that nano-TiO_2 should be added in small quantity for better performance. According to them, adding 1 wt% nanotitanium dioxide would increase the compressive strength by 118%. This quantity could also reduce the porosity from 11% to 9%. They concluded that the finer the pore structure of the concrete is, the higher the resistance of concrete would be against the chloride penetration. Senff et al. (2012) prepared cement samples with 12 wt% nanotitanium dioxides based on a water/binder weight ratio of 0.5 and did rheological and flow table measurements. They found that the torque, yield stress and plastic viscosity of mortars increase significantly by this modification. However, changes in the mechanical properties, such as the compressive strength were not obvious. According to the study carried out by Meng et al. (2012), where 0 wt%, 5 wt% and 10 wt% nano-TiO_2 were mixed by the cement, the lowest compressive strength was observed in the sample with 10 wt% nanotitanium dioxides. A very same conclusion was drawn by Perez-Nicolas et al. (2017) where it was found that after 28 days of curing, increasing the amount of TiO_2 from 0.5 wt% to 2.5 wt% in the cement structure decreases the compressive strength. Chen et al. (2012) used a similar percentage as Meng et al. (2012) and showed that the compressive strength increases at all ages. Mohseni et al. (2016) studied the application of nano-TiO_2 on the integrity of rice hush ash (RHA) based cement. The percentage of nanoparticles was ranging from 0 wt% to 5wt % of the binder and the water to binder ratio of 0.4 was applied to all mixtures. Improvements of the compressive strength and durability were recorded, especially for the mixture with 10 wt% RHA and 5 wt% nano-TiO_2. They indicated that adding nano-TiO_2 and RHA produces C-S-H and decreases the amount of C-H. A very similar experiment was carried out by Praveenkumar et al. (2019) where they replaced Portland cement by nano-TiO_2 to improve the strength and durability performances of concrete after 7, 28 and 90 days. The results revealed that the highest strengths and durability performances is obtained with a combination of 10 wt% RHA and 3 wt% TiO_2 Nanoparticles. Increasing the TiO_2 nanoparticles beyond 3% may drop the strengths and durability properties.

Kadhim et al. (2019) mixed various quantities (0, 0.5, 1.0, 1.5 and 3%) of nano-TiO_2 with the ordinary Portland cement at a constant water to cement ratio of 0.45. A series of tests were carried out, including compressive strength, tensile strength

and water absorption. The authors indicated that nano-TiO_2 can act as a filling agent and activate the pozzolanic reactions which can decrease the porosity, increase the density and improves the strength. It was concluded that adding more than 3.0 wt% nano- TiO_2 to the cement would increase the water absorption and may generate defects in the cement matrix.

2.3.5. Polymer/Clay nanocomposites

Nano-clay is another promising alternative for the modification of the cement, due to its low price and huge functionalities. It is categorized as a highly purified magnesium aluminum silicate, which can improve the performance of the cement and concretes (Meng et al., 2019; Shama et al., 2019). Hakamy et al. (2014) carried out an experimental study on hemp fabric-reinforced nanocomposites by partially substituting ordinary Portland cement with 1 wt%, 2 wt% and 3 wt% nano-clay. The water to cement ratio was considered as 0.48. It was found that 1 wt% nano-clay would be the optimum quantity to improve the hemp-fabric, nanomatrix adhesion and thermal stability of the cement while it can also reduce the porosity.

Hakamy et al. (2014) studied the cement nanocomposites reinforced by calcined nanoclay (CNC) under NaOH treatment. They reported that 1 wt% CNC could reduce the porosity and water absorption by 12.4% and 14% respectively. CNC was also able to improve the density, flexural strength, fracture toughness, impact strength and thermal stability. In a similar study, Surendra et al. (2015) indicated that nano-clay has a two-layer structure which helps to block the water molecules transport and reduce the permeability of the cement mortar, thereby increasing the compressive strength by 12%. The flexural strength of the cement also increased when 1 wt% kaolinite was added to the cement. Baueregger et al. (2015) studied the use of nano-kaolin clay on the early cement strength development. Their results showed that nano-kaolin clay can boost the early compressive and tensile strengths without posing any negative impacts on the final strength after 28 days. They also pointed out that a proper dispersion technique and an optimum size selection would be critical to improve the overall performance of the cement. These conclusions were consistent with the findings reported by Irshidat and Al-Saleh (2018). They replaced the cement with 0.5 wt%, 1 wt%, and 2 wt% nanoclay. The results showed that adding

a small amount of nanoclay could improve the cement's mechanical strengths, elongate the setting time and reduce the amount of water needed to reach the consistency. They indicated that increasing the replacement level of nanoclay more than 2 wt% could increase the amount of water needed to reach the standard consistency in the cement, which can significantly reduce the flowability of the pastes.

Dejaeghere et al. (2019) examined the dosages of nano-clay and superplasticizer on the cement's rheological properties and compressive strength. They replaced cement by nano-clay with various quantities ranging from 0.5% to 2.5%. It was found that nano-clay reduces the mini-slump and flowability of the cement due to the floc formation of nano-clay. They also indicated that below certain dosages, increasing the dosage of superplasticizer could negatively impact on the compressive strength. The best result was reported for the cement with 1.25 wt% nano-clay with superplasticizer. They concluded that mixing nano-clay superplasticizer is very complicated as these additives are sensitive to the mixture conditions.

2.3.6. Carbon nanotube (CNTs)

Carbon nano tubes (CNTs) are hollow tubular channels, which are a rolled-up version of the single or multiple layer graphene (Ferro et al., 2011). Graphene is a single, thin layer of graphite which can be found in the pencil lead. Sedaghat et al. (2014) found that the incorporation of graphene improves the thermal properties of the hydrated cement, and could reduce the chance of early thermal cracking. CNTs are made of graphene and are often in micrometre size while their diameters are something between 0.4 nm to 10 nm for a single-walled CNT (SWCNT) or from 4 nm to 100 nm for a multi-walled CNT (MWCNT). Figure 2.1 shows a schematic view of SWCNT and MWCNT.

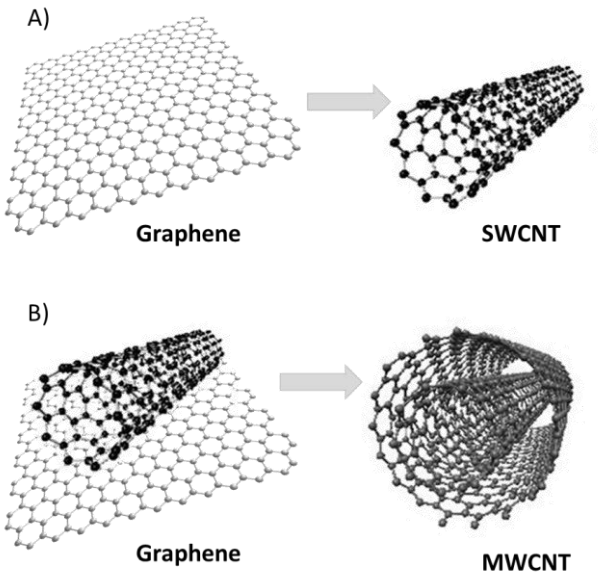


Figure 2.1: A) SWCNT and B) MWCNT structures (modified after www.nanocarbon.cz)

CNTs were discovered by Iijima (1991) as materials exhibiting outstanding mechanical, thermal and conductive characteristics. Since then, this ultralight material has been involved in a variety of different studies related to medicinal, constructions or buildings of structures. There have also been few studies on the application of CNTs in the oil well cementing, where improvement of the compressive strength (Nasibulina et al., 2010), ductility (Abu Al-Rub et al., 2012), and Young's modulus (Sáez de Ibarra et al., 2006) were reported.

Tyson et al. (2011) indicated that CNT can increase the fracture toughness and prevents the creation of crack induced due to the expansion. Ultrasonic mixing was applied to mix the cement and CNT. Based on the cryo-TEM image, it was shown that a poor dispersion would cause friction between particles, agglomeration and reduction in the overall performance of the cement. It was also found that the rheology and stability of the cement slurry will not be altered if a sophisticated dispersion technique is employed (de Paula et al., 2014).

Moreover, CNTs can increase the stiffness of C-S-H and decrease the porosity of the cement matrix, which ultimately reinforce the cement (Ferro et al., 2011). Rahimirad and Baghbadorani (2012) studied the use of CNT reinforced cements in preventing gas migration, as one of the major problems in gas wells. They concluded that the

probability of having casing failure in oil and gas wells can be reduced because CNT has a high aspect ratio and, as such would reduce the chance of crack propagation around a tube. However, to have an efficient synthesized cement, a proper dispersion technique must be applied on an optimum quantity of CNTs. de Paula et al. (2014) dispersed single-layered carbon nanotubes (SWCNTs) into the ground cement clinker using lignosulfonate. Although the results were promising, the scanning electron microscopic images did not show the perfect bonds between the cement matrix and the SWCNTs, which indicate the inefficiency of the dispersion technique applied. Mendoza et al. (2016) indicated that adding MWCNTs by the mass of cement up to 0.5% in an anionic surfactant can help to have a good dispersion. There was no negative impact or chemical affinity with the cement matrix in that study, even at the temperature of 65 ^{o}C. Szelag (2019) studied the cracking potential of the cement modified by MWCNTs, exposed to a significant temperature variation. MWCNTs were dispersed in the presence of a surfactant and sodium dodecyl sulfate (SDS), resulting in the formation of foams during mechanical mixing. The result obtained showed a significant reduction in the cement density and increased in the porosity. They concluded that the combination of MWCNTs and anionic surfactant (SDS) would deteriorate the cement strength.

Naqi et al. (2019) suggested using silica fume particles to improve the MWCNTs dispersion. They prepared a total number of eight samples with different quantities of MWCNTs. The amount of silica fume in each sample was fixed at 10% by the weight of binder. It was observed that silica fume could effectively break the agglomerates of MWCNTs once added to the slurry during dispersion. They concluded that to have maximum strength development, the amount of MWCNTs should not be more than 0.03 wt.%. This was mainly because the entangled and clumped MWCNTs were unable to fill up the smaller pores within the cement paste.

2.3.7. Nano Glass Flake (NGFs)

Glass flake (GF) substrates are defined as highly planar platelets with a very smooth surface. They are transparent with a transparent colour tone. Nano Glass Flakes (NGFs) have been introduced early in 2010, with a thickness of 100 nm to 750 nm. Because of their layered structure, GFs can provide a better interaction between filler

and matrix, which could improve the overall performance of the cement product (Nematollahi et al., 2010; Salehi et al., 2017). Figure 2.2 shows how NGFs can create a tortuous path and prevent the intrusion of gas/liquid inside the cement.

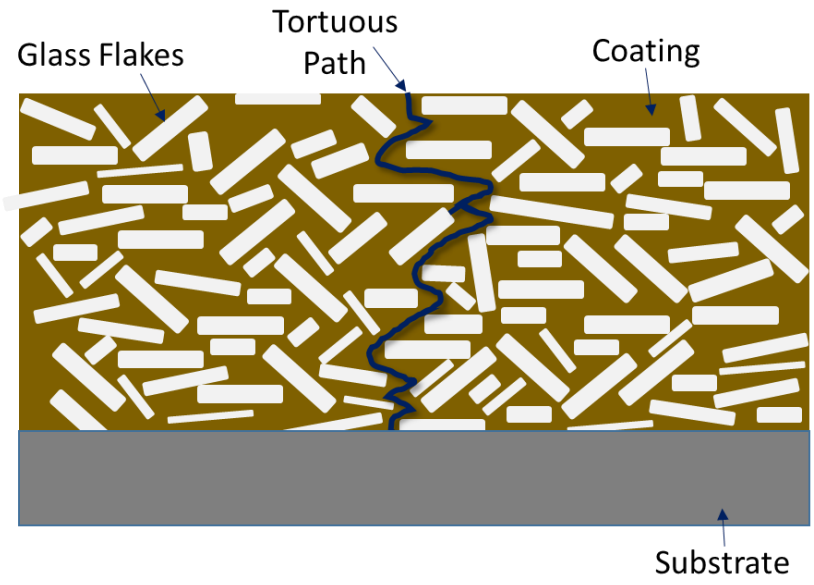


Figure 2.2: Appearance of GFs in a coated substrate (modified from http://www.ktechglobal.in/)

As it is seen in Figure 2.2, the laminar structure of NGFs can create a tortuous path, preventing any particles/gas/liquid to intrude into the substrate easily. NGFs can also improve the chemical and corrosion resistance of materials once properly dispersed in their matrix (Nematollahi et al., 2010; Ghadami et al., 2014). Moreover, they have been extensively used as an in-situ barrier for many industrial applications such as external coating of high temperature oil flow lines in Duri Oil Field, Indonesia. Watkinson (2009) in his study on the concrete indicated that NGFs are capable of enhancing the chemical resistance, compressive and tensile strengths of the cement while they are extremely good for long-term protection. According to Salehi et al. (2017), adding 0.5 wt. % GFs would be the best quantity to maintain the cost of the cementing operation and improve the tensile strength of the Portland cement although caution must be taken to ensure that NGFs is properly dispersed in the cement matrix (Arabi et al. 2018; Guo et al. 2018).

Up to date, a limited number of researches carried out on the application of NGFs in oil well cementing. Nevertheless, glass powder (GP) has been considered in several

studies, which has similar chemical properties as glass flakes. Elaqra and Rustom (2018) prepared glass powder (GP) from crushed local glass sheets and broken pieces collected from a landfill, with the size of less than 75 µm. They discovered that GP could improve the formation of C-S-H and compressive strength at the late ages. As the amount of GP increases, more hydrate products would be formed and as such the cement is densified.

Cai et al (2019) studied the effect of nano-silica and waste glass powder (WGP) on the swelling of the cement caused by alkali-silica reaction (ASR). WGP was obtained from the ball milling process of recycled waste glass gullet, producing particles with the size of less than 5mm. Compared to the control sample, the samples with 10% WGP had the highest reduction of swelling after 14 days. It was also observed that WGP can increase the bulb resistance which could be due to the limited formation of microcracks in the cement matrix. Improvement of the strength was also noted in the cements with WGP which could be due to limited expansion and continuous pozzolanic reactions. Table 2.2 gives a summary on the application of nanomaterials in the cement industry.

Table 2.2: Application of nanomaterial in the cement industry (Lee, 2012)

Nanomaterials	Effect on the cement
Nanosilica (nano-SiO_2)	• Improving the strength and workability. • Accelerating hydration due to the surface area. Improving the microstructure due to filler effect reductions in setting time
Nano-iron (nano-Fe_2O_3)	• Improving the concrete strength. • Enhancing the self-monitoring capabilities
Nano-alumina (nano-Al_2O_3)	• Abrasion resistance improvement • Ability to sustain any drastic changes in temperature • Improving the compressive strength and elastic modulus
Nano-titanium dioxide (nano-TiO_2)	• Removal of volatile organic compounds and self-cleaning. • Accelerating the early-age hydration and increasing the compressive and flexural strengths

	• Improvement in resistance to flame, corrosion and abrasion.
Polymer/clay nanocomposites	• Increasing the tensile strength and heat resistance. • Reducing the oxygen permeability.
Carbon nanotube (CNT)	• Controlling the matrix cracks at the nanoscale level. • Improving the compressive, tensile, flexural and bending strengths, and hence enhance the durability. • Because of its size and aspect ratios, it can result in a more efficient crack bridging.
Nano glass flake (NGF)	• Enhancing the chemical and abrasion resistance. • Improving tensile, compressive and flexural modulus.

Given the advantages of Carbon Nano Tubes (CNTs) and Nano Glass Flakes (NGFs), which have been highlighted in the civil industry, these two nanomaterials were selected in this study to examine their application in the oil well cementing used for CO_2 storage sites. Similar to other nanomaterials, both of them can improve the cement strength and durability. In addition, they having better resistance against temperature, pressure and corrosive environments. It worth to mention that NGFs has been rarely used for the enhancement of well cementing. Due to its salient features, studying the effect of NGFs on the cement could be significant. On the other hand, although CNTs have been widely used in the cement related studies, its application as an additive to improve the cement performance in CO_2 storage site has not been widely studied. Nevertheless, the dispersion of nanoparticles could be a big problem since their large surface area and strong van der Waals force may cause agglomerates.

In the following chapters, CNTs and NGFs are further introduced and studied to see if they can improve the performance of the cement in CO_2 storage sites.

2.4. Summary

There have been many studies proposing a solution to improve the overall performance of the cements used in CO_2 sequestration site, but these approaches were not totally successful due perhaps to the severity of interactions taking place between the cement and supercritical CO_2. Nanomodification has been reported as a promising approach to improve the physical and mechanical properties of the cement given the huge reactivity of nanoparticles. It seems that almost all types of nanomaterials can act as a filler to densify the microstructure, reduce the porosity, improve the transfer properties and, eventually, enhance the mechanical strength of the cement. However, many of these nanoparticles are either expensive or impossible to properly disperse in the cement matrix. There is also no established approach to determine the quantity of nanoparticles required to have an efficient cement under different reservoir conditions. According to the literature, CNTs and NGFs can be the best choice for nanomodification of the cement used in oil well cementing and CO_2 storage sites.

Chapter 3: Application of Nano Glass Flakes (NGFs) in Well Cementing

3.1. Introduction

Nano glass flakes (NGFs) are considered as one of the best nanoparticles used in many industrial applications (Watkinson, 2009; Ghadami et al., 2014). They are defined as highly planar transparent platelets with a very smooth surface which are generally made of silicon dioxide (SiO_2), sodium oxide (Na_2O), sodium carbonate (Na_2CO_3), calcium oxide (CaO), and some minor additives (Glass Flake Ltd). The laminar structure of NGFs can stop the intruders to enter into substrates by creating a tortuous path. In addition, GFs can resist the chemical degradation and corrosion by providing a strong protective barrier (Nematollahi et al., 2010). As a result, they have been used as a reinforcing filler in the anticorrosive coating (Watkinson, 2009). However, unlike many other nanoparticles such as Carbon Nanotubes (CNTs) and nanosilica (NS), their applications in the oil well cementing have not been widely explored. In fact, the salient features of NGFs, such as extremely high melting point (>930^{o}C), anti-corrosion characteristics, thermal stability and morphological structures make them an attractive candidate for the reinforcement of the cement used under HPHT conditions.

In this chapter, attempts are made to evaluate the application of NGFs in oil well cementing by performing a series of tests on the class G cement. The optimum quantity of NGF and its impacts on the cement structure are also provided and discussed with details.

3.2. Methodology

3.2.1. Cement Composition

For this study, ECR Glassflake unmilled grade GF100nm was used as the additive/replacement for the preparation of the cement samples. It is an innovative ultra-thin ECR glass flake product donated by Glassflake Ltd, with the purity of more than 98% (<2% is saline coupling agent). This NGF has a nominal flake thickness of

100nm and is completely transparent as shown in Figure 3.1. The properties of the NGFs used in this study are listed in Table 3.1.

Table 3.1: Material Properties of NGFs used for this research

Physical Properties	
Density, g/m^3	2.60
Softening temperature, °C	688
Melt temperature, °C	930 - 1020
Refractive index	1.52
Nominal thickness, nm	100
Particle Size Distribution	
1700 - 150 µm	≥ 80%
< 150 µm	≤ 20%
Chemical Characterization	
SiO_2	64 - 70%
Na_2O	8 - 13%
CaO	3 - 7%
Al_2O_3	3 - 6%

For the experimental purpose, the API Class G cement was used as it is commonly used in the oil and gas industry for deep and high-pressure conditions (Lafarge, 2009). Chemical and physical properties of the cement used are summarized in the Table 3.2.

Table 3.2: Chemical and Physical Properties of the Class G Cement (Lafarge, 2009)

Chemical Component, %		Physical Properties	
Magnesium oxide (MgO)	≤ 6.0	Maximum free fluid content, %	5.9
Sulphur Trioxide (SO_3)	≤ 3.0		
Loss on Ignition	≤ 3.0	Blaine specific surface area, m^2/kg	280 – 340
Insoluble Residue	≤ 0.75		
C_3S	≤ 48 – 58		≤ 30 Bc

C_3A	≤ 8.0	Consistency (52°C, 33.6 MPa and 15-30 minutes)	
$C_4AF + 2\ C_3A$	≤ 24		
Equivalent Alkali (Na_2O)	≤ 0.75		

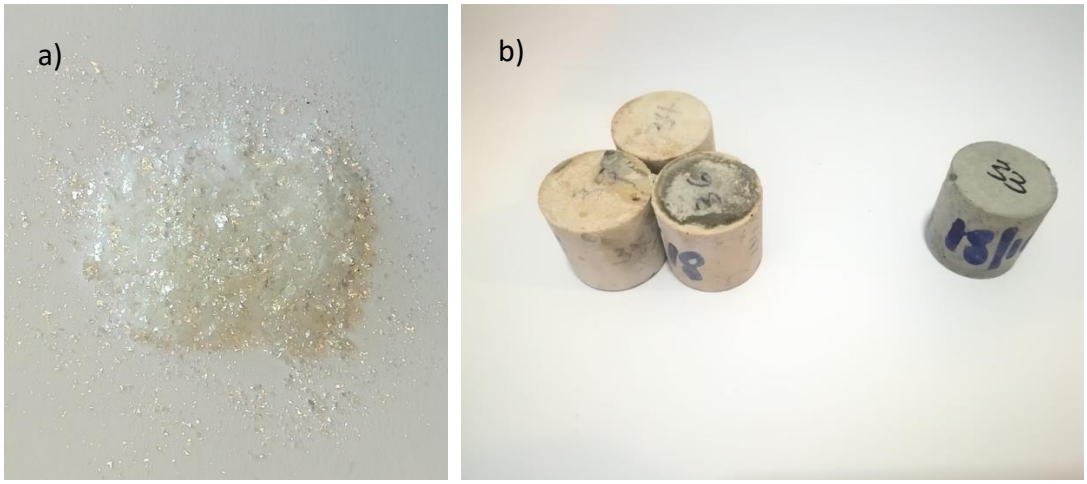


Figure 3.1: a) Physical appearance of NGFs, and b) cement samples modified by NGFs (left) and pure cement (right)

API 10A and 10 B Standards were followed to prepare different cement compositions (See Figure 3.1 right). These standards provide recommendation for the water-to-cement ratio (w/c) and measurements of free fluid, rheology and the compressive strength of the cement samples. Nevertheless, there is no standard procedure developed as a reference to determine the amount of NGFs which can be mixed by the cement for a good performance. There is also no established guideline as to how NGFs can be dispersed into the cement slurry.

Thus, a series of analysis and interpretations were carried out to ensure that NGFs can improve the overall performance of the cement under the reservoir conditions.

3.2.2. Mixing Method

To prepare the cement samples, neat cement (cement without any additives) was mixed with deionised water according to the API Standard 10-A (2005) with a water-to-cement (w/c) ratio of 0.44. This ratio was consistent, even when the NGFs were added into the cement. Two mixing methods were compared, which are

manual/hand mixing (H) and ultrasonication (S). They are further discussed in the next sections.

3.2.2.1. Manual/Hand Mixing Method

To prepare the hand mixing samples, NGFs were added to the cement and hand mixed consistently for 5 minutes. The slurry was then mixed at the speed of 4000 rpm for 15 second, followed by a high-speed mixing at 12,000 rpm for 35 seconds. This approach in this study is referred to as the conventional mixing which is also known as the hand mixing.

3.2.2.2. New Mixing Method

A new mixing method was also developed with the help of LSP-500 Ultrasonic Processor (Industrial Sonomechanics), where NGFs were treated and dispersed in deionised water before being adding into the cement. The ultrasonication was done at 500 Wt and 20 KHz, with an amplitude of 50% for 15 min. During the sonication, every 20 sec, the processor stopped for 5 sec in order to avoid overheating (Konsta-Gdoutos et al, 2010). The results obtained indicated that this approach can prevent particle aggregation.

However, the heat generated from the process may lead to a certain level of water loss. Hence, the water loss was compensated prior to the next stage. This approach is referred to as the new mixing or sonication technique in this report. In the end, six sets of samples were prepared as reported in Table 3.3.

Table 3.3: Cement samples prepared with different amount of NGFs

Sample No.	NGFs Content (wt.%)	Weight of NGFs, (g)	Weight of Cement, (g)	Weight of Water (g)
1	0	0	592.00	260.48
2	0.05	0.30	591.70	260.48
3	0.25	1.48	580.52	260.48
4	0.50	2.96	589.04	260.48
5	0.75	4.44	587.56	260.48
6	1.00	5.92	586.08	260.48

The overall process of mixing is summarized in Figure 3.2. Table 3.4 gives the list of the tests conducted on the samples upon preparation and the workflow is presented in Figure 3.3.

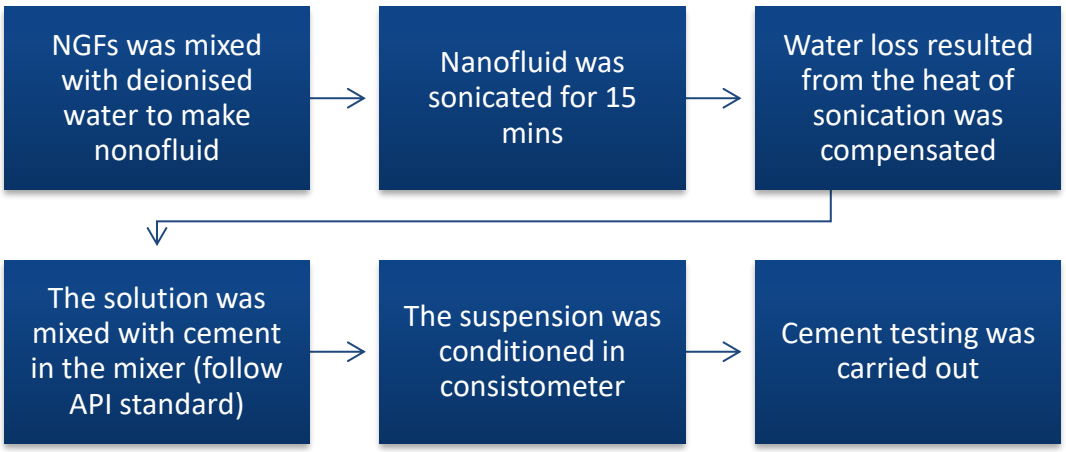


Figure 3.2: A flow chart showing the steps taken to prepare the cement samples

Table 3.4: The list and objectives of the tests conducted on the cement samples

Tests	Equipment	Objective
Zeta Potential	Malvern Zetadizer NanoZS	To identify nanoparticles' surface charge
Rheology	Fann model 35 Rotational Viscometer	To determine viscosity of cement
Density	Fann Mud Balance TruWate Model 141	To determine density of cement
Free Fluid	-	To measure the free water of cement after setting
Uniaxial Compression	Ultrasonic Cement Analyzer (UCA)	To measure non-destructive compressive strength
Uniaxial Compression	Universal Testing Machine (UTM)	To measure destructive compressive strength
Thermogravimetric Analysis	Mettler Toledo Thermogravimetric Analysis (TGA)	To find out the percentage loss of Portlandite
X-Ray Diffraction Analysis	Bruker D2 PHASER	To identify the phase of cement hydration.

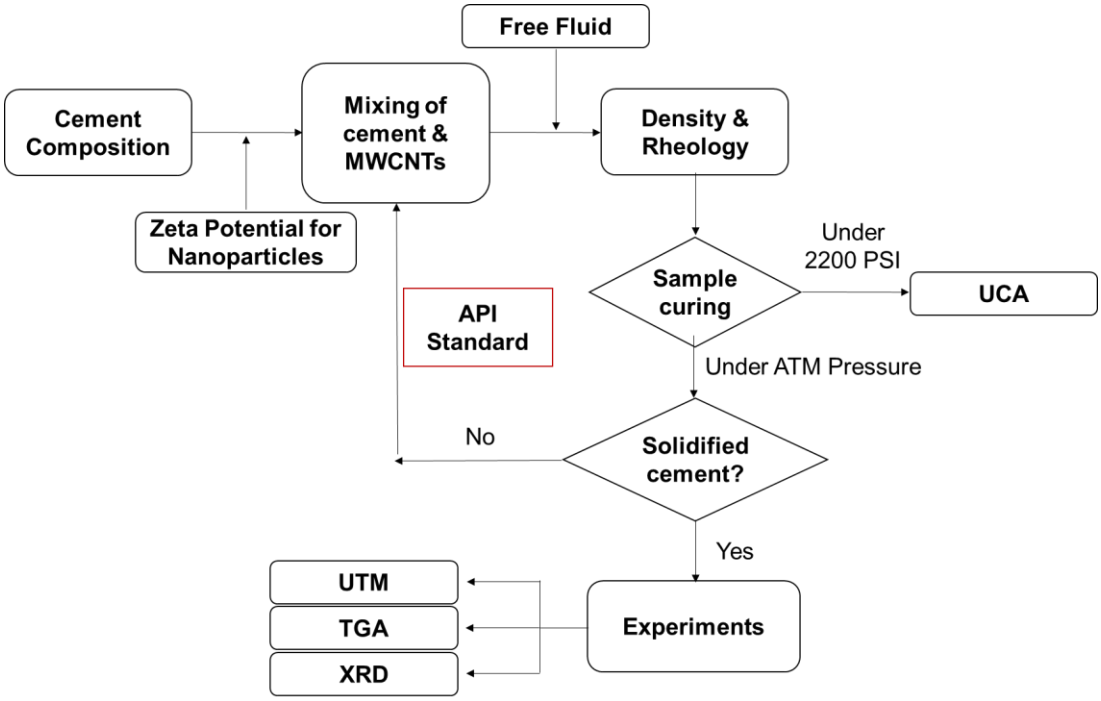


Figure 3.3: The workflow of the methodology

3.3. Experimental Results

3.3.1. Zeta Potential

Zeta potential indicates the net surface charge of nanoparticles. As a matter of fact, by determination of the surface charge of nanoparticles, their physical state in the solution can be assessed and their stability is obtained (Risnes et al., 2005). The term stability here is referred to as the tendency of particles to aggregate in an aqueous medium. Usually, during a zeta potential measurement, an electric field is applied, inducing movement for the charged particles. The ratio between the velocity of nanoparticles and the applied electric field in the solution, which is also known as electrophoretic mobility, is then measured. This mobility can be converted into zeta potential (z) using the Henry function expressed below:

$$\mu_e = 2\varepsilon \times z \times f(k\alpha)/3\eta \quad (3.1)$$

In the above equation, ε is the dielectric constant, η is the zero-shear velocity of the medium, f(kα) is the Henry function, α is the radius of the particles and k is the thickness of the electrical layer which is linked to the ionic strength and the temperature of the medium.

For the purpose of this study, Marven ZetaSizer Nano ZS instrument was used to measure the zeta potential of the solutions with NGFs. The sensitivity of the solution to the variation of pH was also tested as shown in Figure 3.4. Changes in pH were obtained by adding HCl and NaOH to the dispersed solution.

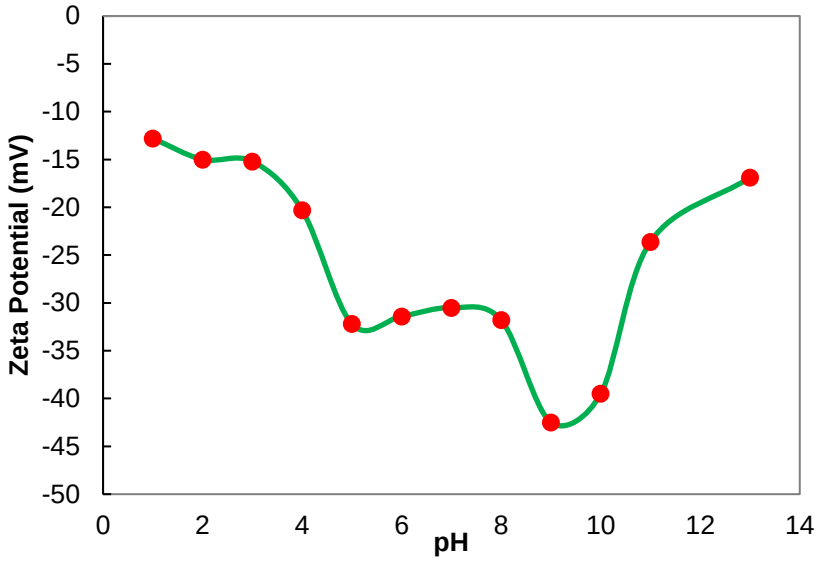


Figure 3.4: Zeta potential of NGFs at different pH conditions

The results obtained indicated that NGFs are negatively charged at the room temperature of 25^{o}C. It appears that they have a strong negative surface charge of more than -30 mV when the pH varies from 5 to 11. At the pH of 9, the solution has the highest negative charge value of -43 mV. It was concluded that NGFs are much stable in an alkaline environment, although they have favourable negative surface charges under acidic conditions. This would indicate that if the cement samples can be prepared under the pH of 9, the maximum stability of nanoparticles can be achieved for a better performance and dispersion.

3.3.2. Density

Measuring the density of the cement slurry is crucial to ensure that lost circulation can be prevented during placement in unconsolidated and weak formations (Shariah, 2011). After mixing and preparation, the density of the cement slurries was measured using the Fann Mud Balance TruWate Model 141 with a pressurized cup. Before this, the mud balance was calibrated according to the manual instruction of Fann. This cup was used to release entrained air could be released they may reduce

the accuracy of the density measurements. This was done by covering the cup with the lid and applying pressure through a syringe by which the slurry could be expelled through the check valve. Table 3.5 gives the density measurements made for both hand-mixed and sonicated cement samples.

Table 3.5: Density of the cements prepared through hand mixing (H) and sonication(S)

wt. (%)	NGFs (H), g/cm^3	NGFs (S), g/cm^3
0 (0)	1.78	1.78
0.05	1.78	1.78
0.25	1.8	1.79
0.50	1.81	1.78
0.75	1.81	1.81
1	1.79	1.82

As it is seen in Table 3.5, although the cements were replaced by the nanoparticles, their density did not significantly change and is still within the range of 1.78 to 1.82 g/cm^3. It seems that the samples prepared through the hand mixing and sonication are giving a similar result which is very close to that of the neat cement. It was then concluded that the mixing method does not have any impact(s) on the cement density.

3.3.3. Rheology

Typically, rheological studies are done to determine the inherent fluid properties, particularly viscosity. Viscosity is the parameter that defines the relationship between the shear rate and pressure gradient (shear stress) that creates fluid movement (Guillot, 2006). Yield point is another term in the rheological context, described as the shear stress that must be applied to put the slurry into motion. In principle, the science of rheology is employed to evaluate the pumpability of the cement slurry and the frictional pressure loss during placement (Shariah, 2011). It is also related to the thickening time of the cement before being consolidated.

To determine the rheological behaviour of the cement, the rotational viscometer of Fann model 35 was used. In this practice, the cement slurries were placed in the

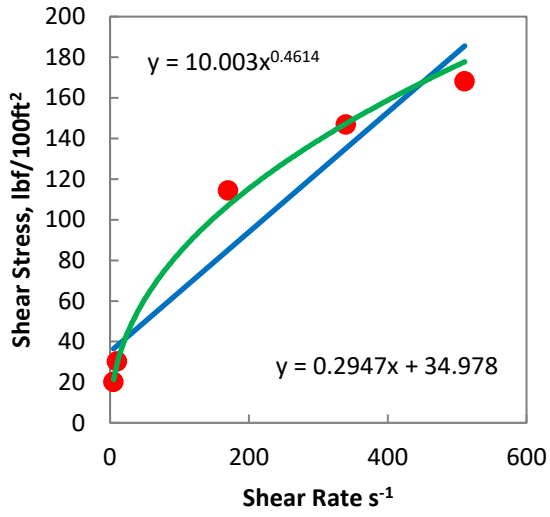
shear gap between the outer cylinder and the bob (inner cylinder). Each sample was sheared at 3rpm and the initial dial reading was taken after 10s. All the remaining dial readings were then taken except for 600rpm in the ascending (ramp-up) and descending (ramp-down) orders. The ratio of the dial readings during ramp-up and ramp-down at each speed was close to 1:1 to ensure that the fluid is in the nonsettling or nongelling state.

Two common mathematical models used in the industry to determine the rheological behaviour of the cement are Power law and Bingham plastic. Among these two, Bingham plastic is the primary model due to its linear nature and proven applications. Plastic viscosity and yield point are the slope and the intercept of the graph created after plotting the shear rate against the shear stress in the Bingham law. On the other hand, the power law model is represented by two parameters, consistency index (k) and behavior index (n), which respectively indicate the apparent viscosity and the degree of the non-Newtonian behaviour in the cement slurry. For determination of the rheological behaviour, the API 10-B guideline was followed. The results obtained from the rheological measurements of the hand-mixed and sonicated NGFs cements are summarized in Table 3.6, Figure 3.5, Table 3.7 and Figure 3.6. It should be noted that each test was repeated twice for the same cement composition to ensure the consistency of the results.

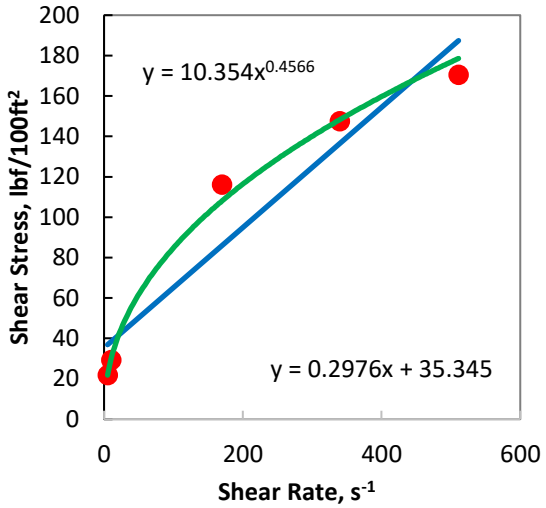
Table 3.6: Rheological properties obtained for the samples prepared by the manual mixing approach

NGF content, wt.%	Viscosity, cP	Yield Point, lb/100ft^2	K, lbf.s^n/ft^2	n
0.00	141.17	34.978	0.1000	0.4614
0.05	143.15	35.345	0.1035	0.4566
0.25	146.90	36.420	0.1058	0.4582
0.50	175.50	37.627	0.0932	0.5034
0.75	202.80	34.431	0.0732	0.5621
1.00	213.40	50.723	0.1524	0.4567

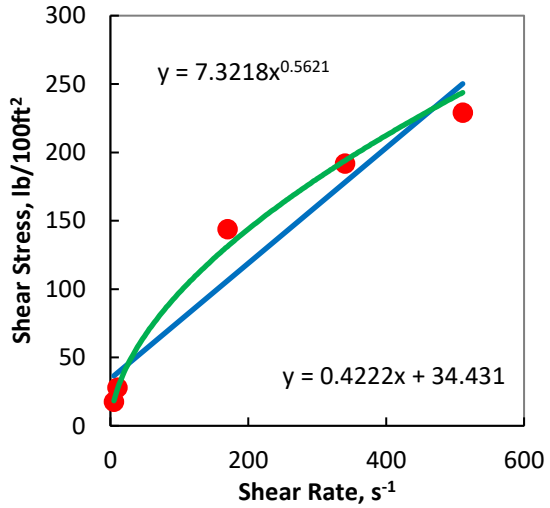
Neat Cement



0.05 wt. % (H)



0.75 wt. % (H)



1.00 wt. % (H)

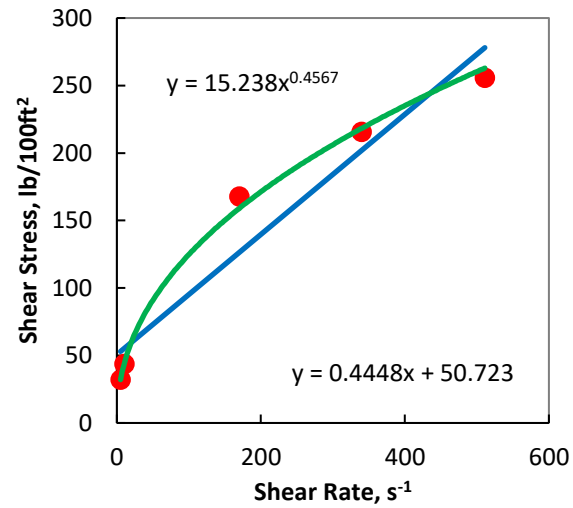
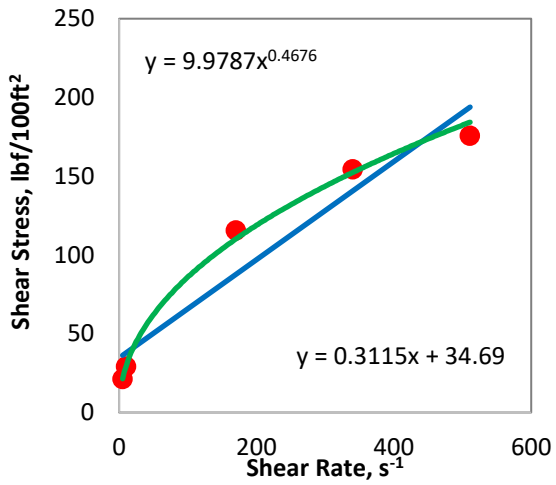


Figure 3.5: Rheological parameters and models obtained for the samples prepared by the hand mixing method

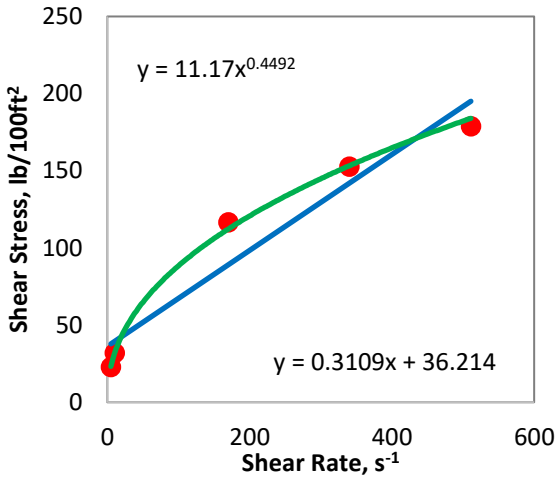
Table 3.7: Rheological properties obtained for the samples prepared by the sonication method

NGF content, wt.%	Viscosity, cP	Yield Point, lb/100ft^2	K, lbf.s^n/ft^2	n
0.00	141.17	34.978	0.1000	0.4614
0.05	145.27	34.69	0.0999	0.4676
0.25	149.10	36.214	0.1117	0.4492
0.50	190.30	36.467	0.0808	0.5339
0.75	209.10	35.114	0.07718	0.5571
1.00	234.80	39.043	0.08471	0.5607

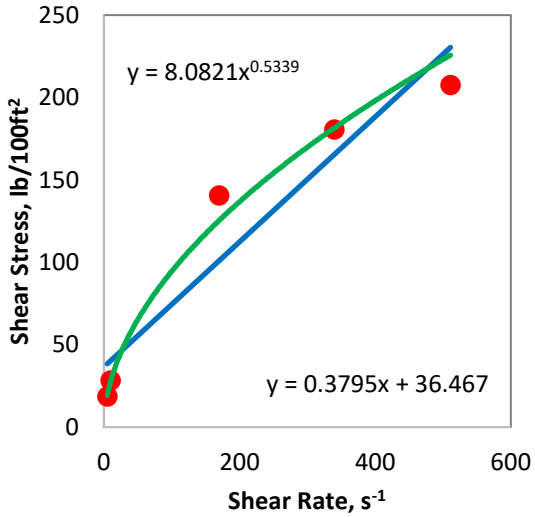
0.05 wt. % (S)



0.25 wt.% (S)



0.50 wt.% (S)



1.00 wt.% (S)

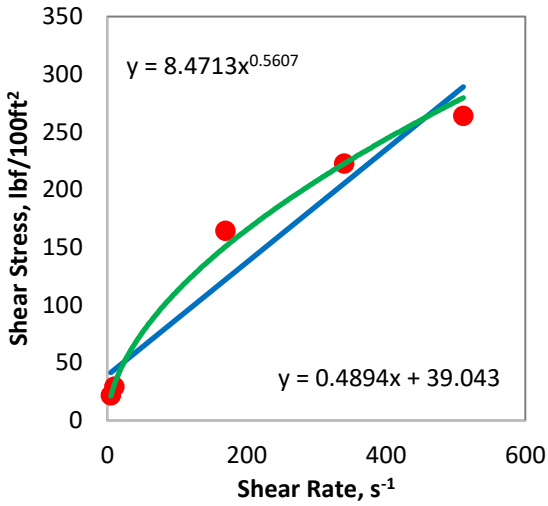


Figure 3.6: Rheological parameters and models obtained for the samples prepared by the sonication method

It is seen from both tables that the higher the amount of NGFs replaced with the cement, the higher the viscosities of the cement slurry would be. The trend of rising is very similar for both hand mixed and sonicated samples. It seems that when the amount of NGFs in the cement goes higher than 0.25 wt. %, the viscosity increases sharply, from ~150 cp to ~190 cp. For the sonicated samples, this increase in the viscosity is even higher with the highest value reported for the cement samples with 1 wt. % NGFs.

This could be due to the water loss induced by the ultrasonic processor by which the temperature of the solution increases from room temperature to ~60^{o}C because of mechanical vibration. Although attempts were made to compensate the water loss, the heat generated can still accelerate the cement hydration, decrease the cement paste fluidity and eventually affect the viscosity (Hielscher, 2006; Golaszewski and Cygan, 2009). On the other hand, the hand-mixed samples have a comparatively lower viscosity which could be due to the poor integration between the cement and nanoparticles. In fact, particles of NGFs can be bounded together into macroscopic structures by Van der Waals forces forming agglomerates without a proper dispersion (Taurozzi et al., 2010). Due to the presence of agglomerates, the molecules of the substances are unable to mix homogenously, resulting in a higher mobility.

From the result obtained, it appeared that as the replacement ratio of NGFs increases, the yield stress increases. The yield stresses for the samples with different mixing methods are similar in a low replacement ratio of 0.25 wt%. However, as the concentration of NGFs increases to 0.5 wt. %, the yield stress changes from 35 lb/ft^2 to 40 lb/ft^2. According to Yim et al (2016), the particle distribution is a crucial factor and can change the yield stress under different conditions. This also verifies the fact that a proper dispersion method should be employed to accurately determine the rheological behaviour of nano modified cements.

3.3.4. Free Fluid

Free fluid is defined as the amount of water appears on the top of the cement slurry upon mixing and is not used for the hydration. There is a procedure that can be followed to determine the free water as per the API 10A standard. According to this standard, once the cement slurry is standing in a static condition, free water will accumulate on the top of the cement slurry. This free fluid must be measured to ensure that channel and leakage paths will not be induced during the hydration. The amount of free fluid for the class G cement should be less than 5.9% as per the API recommendation practices.

To determine the amount of free water in this study, the cement slurry was stirred for 20 min at the speed of 150 rpm under the temperature of 27 ^{o}C in a

consistometer. The volume of the fluid was measured after 2 hours by the accuracy of ± 0.1 ml. These measurements were then converted into the percentage using the following equation:

$$\%ff = \frac{V_{ff} \times \rho}{m_s} \times 100 \quad (3.2)$$

where %ff is the percentage of free fluid, V_{ff} is the volume of the free fluid, p is the specific gravity of the slurry and m_s is the initial mass of the cement slurry that is transferred into the conical flask. The results obtained are presented in Figure 3.7 and summarized in Table 3.8.

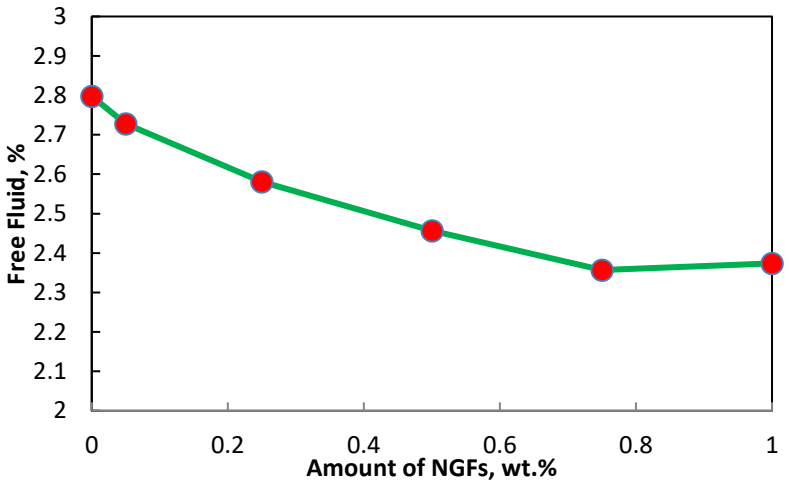


Figure 3.7: Free fluid vs concentration of NGFs

Table 3.8: Free fluids obtained from the NGFs-cement nanocomposites after 2 hours

Amount of NGFs, wt.%	Mass of cement, g	Volume of Fluid, ml	Density, g/cm^3	Free Fluid, %
0	763.5	12.00	1.78	2.80
0.05	763.48	11.70	1.78	2.68
0.25	762.97	11.00	1.79	2.58
0.50	760.83	10.50	1.78	2.46
0.75	763.70	10.10	1.80	2.36
1	762.52	10.00	1.81	2.37

It should be recalled that nanoparticles are often hydrophilic and can increase the amount of water adsorption. In fact, the higher the quantity of NGFs in the cement, the lower the amount of free fluid would be. This was aligned with the study of Nematollahi et al. (2010) who carried out the water absorption test (ASTM D570 specification) on the NGFs modified epoxy resin at the curing temperature of 60 °C for 1 week. They concluded that as the amount of NGFs increases, the water absorption increases. However, when the concentration of NGFs exceeds 0.5 wt. %, the free water level does not drop and would rather rise. This could be due to the formation of nano agglomerates. Thus, once the amount of NGFs exceeds a certain quantity, a better dispersion method would be needed to avoid the agglomeration induced by the interfacial forces.

3.3.5. Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) was used to determine the weight loss of calcium hydroxide (CH) within the cement samples. This loss is also known as the dehydroxylation of Portlandite. In this study, the following operational conditions were considered for running the TGA (Garnier et al., 2010):

- Starting temperature: 25°C;
- Ending Temperature: 600°C;
- Heating Rate: 10°C/min;
- Temperature for dehydroxylation of portlandite: 400 to 500°C;
- Gas Flow Rate: 50mL/min;
- Type of Gas: Nitrogen (flow rate of 50ml);
- Sample Weight: 10mg.

The amount of portlandite left in the samples was measured using the following equation:

$$CH\ (\%) = WL_{(CH)}\ (\%) * MW_{(CH)}/MW_{(H)} \quad (3.3)$$

where CH is referred to as the amount of portlandite left in the samples, $WL_{(CH)}$ is the percentage loss of Portlandite during dehydroxylation, $MW_{(CH)}$ is the molecular weight of Portlandite and $MW_{(H)}$ is the molecular weight of water. In the next section,

the results obtained from the TGA under different conditions are discussed and explained in details.

3.3.5.1. Different Mixing Methods

Two mixing methods (hand mixing (H) and sonication (S)) were used to prepare samples with 0.5 wt.% NGFs. TGA was then ran on the samples to quantify the amount of the weight loss. These samples were cured in a water bath under the temperature of 50°C. The results obtained are given in Table 3.9 and shown in Figure 3.8.

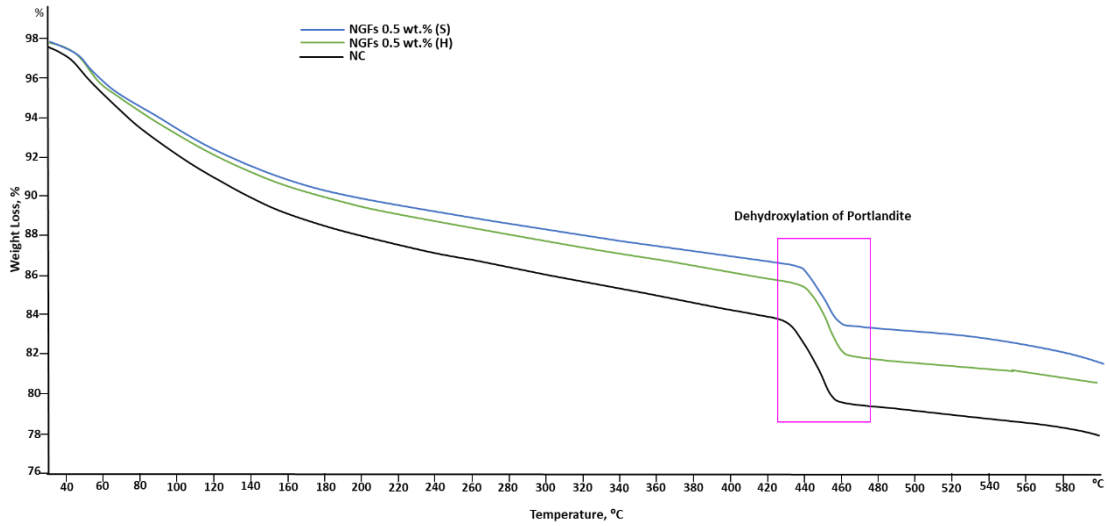


Figure 3.8: TGA plots comparing the dehydroxylation of the neat cement and the samples with 0.5 wt.% NGFs

Table 3.9: Weight loss and the amount of portlandite left in the NGFs based cements

NGFs Content, wt. %	0	0.5 (H)	0.5 (S)
Weight Loss, %	4.50	3.95	3.25
Portlandite, %	18.51	16.26	13.35

Looking at Table 3.9, it is seen that the neat cement has the highest weight loss of close to 4.5% which corresponds to the presence of 18.5% portlandite. Replacement of the cement with NGFs, even though the amount was only 0.5 wt%, could reduce the production of portlandite and generates more C-S-H. It was also observed that the sonicated (S) sample has the least weight loss (3.25%) compared to the conventional hand-mixed (H) samples (3.95%). Reduction of Portlandite would

indicate that a better resistance might be provided by the cements once exposed to CO_2 given the fact that portlandite is an alkaline component and would be attacked by CO_2 very rapidly.

This result was also confirmed that that sonication used to disperse nanoparticles can improve the interaction between NGFs and the cement. As a result, NGFs could fill up the pore spaces within the cement and increases the strength. This is aligned with the result obtained from the non-destructive and destructive tests where it was found that the compressive strength of the sonicated samples is generally higher than the samples prepared by the hand mixing method.

3.3.5.2. Different Curing Conditions

To investigate the effect of pressure and temperature on the cement hydration, 0.5 wt.% NGFs cement samples were used. The hand mixed and the sonicated samples were then compared under: 1) the temperature of 50°C and the pressure of ~16MPa (UCA); 2) the temperature of 50°C and the atmospheric pressure. The temperature was kept constant in order to evaluate the influence of pressure on the cement. The result obtained is shown in Figure 3.9 and given in Table 3.10.

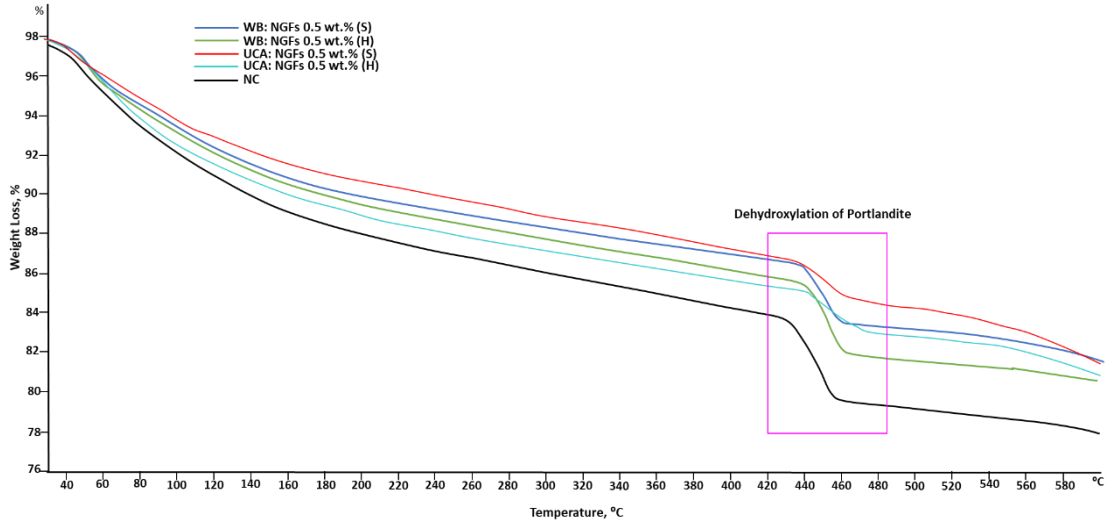


Figure 3.9: TGA plot of 0.5 wt.% NGFs cement samples with different mixing methods and curing conditions

Table 3.10: Weight loss of NGFs cement with different mixing methods and curing conditions

NGFs Content, wt. %	0.5 wt.% (H)		0.5 wt.% (S)	
Curing Condition	Water Bath (WB)	UCA	Water Bath (WB)	UCA
Weight Loss, %	3.95	2.27	3.25	2.23
Portlandite, %	16.26	9.33	13.35	9.17

It was revealed that the samples cured under the UCA condition have a lesser amount of Portlandite than those cured under the water bath condition. This could be linked to the effect of the pressure which increases the production of secondary C-S-H and reduces the amount of Portlandite. It is also believed that the additional reaction with NGFs consumes the Portlandite at the early stage of hydration. Based on the literature, curing at the higher pressure would lead to a higher degree of hydration which results in a denser C-S-H and thereby enhancing the silicate polymerization of the cement (Burlion et al., 2006; Neville, 2011; Jung et al., 2013).

To further confirm these findings, one more test was done on the samples with 1 wt.% NGFs and 0.5 wt.% NGFs prepared by the sonicated method. The results obtained presented is given in Table 3.11 and shown in Figure 3.10. It appears again that the samples cured in the UCA have a lesser amount of portlandite than those cured in the water bath. It was also observed that the sample with 0.5 wt.% NGFs cured in the UCA produces the least amount of portlandite. This highlights that pressure has a huge impact on the production/consumption of portlandite in the cement where due to a better reaction of NGFs with the cement, more C-S-H could be produced.

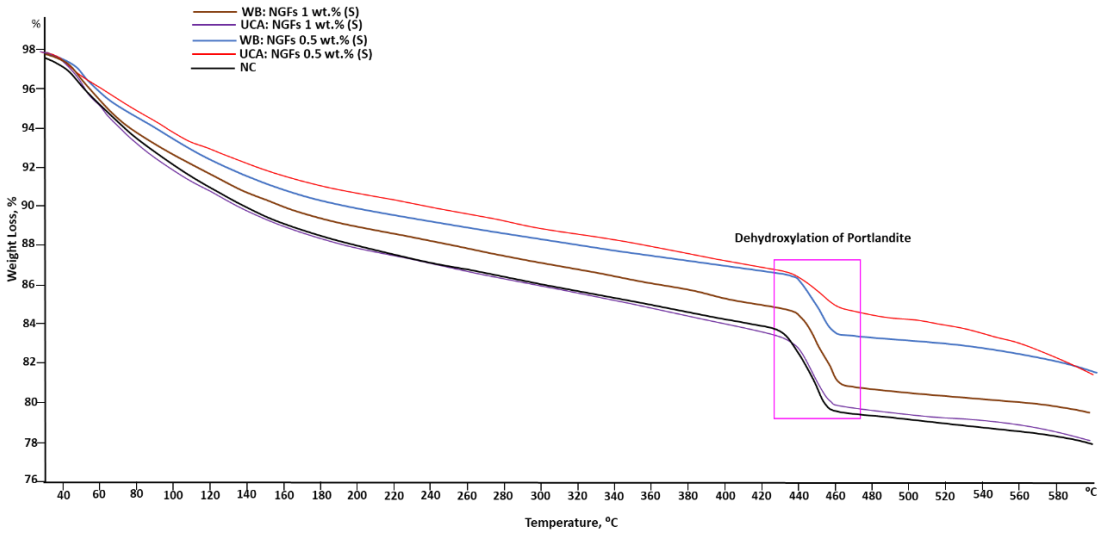


Figure 3.10: TGA plot of 0.5 wt% and 1 wt.% of NGFs (S) samples under different curing conditions

Table 3.11: Weight loss and presence of Portlandite in the samples with NGFs

NGFs Content, wt. %	0.5 (S)		1 (S)	
Curing Condition	Water Bath	UCA	Water Bath	UCA
Weight Loss, %	3.25	2.23	4.08	3.79
Portlandite, %	13.35	9.17	16.79	15.60

3.3.6. Compressive Strength

Compressive strength is another important property which indicates the maximum stress sustained by the consolidated cement before failure. Two different measurements were made to determine the strengths of the cement which include destructive and non-destructive tests. In this section, these two measurements are discussed in details.

3.3.6.1. Non-Destructive Test

To determine the development of the compressive strength over time, Ultrasonic Cement Analyser Model 3504 was used (See Figure 3.11). This apparatus is capable

of providing an initial set time (i.e., the time needed for the cement to achieve the compressive strength of 50 PSI/0.35 MPa) and Waiting On Cement (WOC) (i.e., the time required for the cement to reach the compressive strength of 500 PSI/3.45 MPa). UCA was operated at 2200 PSI (15 MPa) and 50^{o}C for 24 hours to simulate the real reservoir condition. Figure 3.12 shows the results obtained for the WOC measurements.

Figure 3.11: Ultrasonic Cement Analyser Model 3504 used for the purpose of this study

As shown in Figure 3.12, regardless of the mixing methods, the WOC of the cement samples with NGFs is shorter than that of the neat cement. Comparing the hand mixing and the sonicated samples, it appeared that the sonicated samples give a shorter WOC time due to the rapid strength developments. This further confirms the need for a good dispersion method to promote hydration and strength development. The results obtained from the measurement of the cement strength, which are shown in Figure 3.13, also highlighted that the sample with 0.5 wt.% NGFs would be the best option to have the highest strength in a short period of time. Figure 3.14 shows the strength development of the sonicated samples obtained from the UCA.

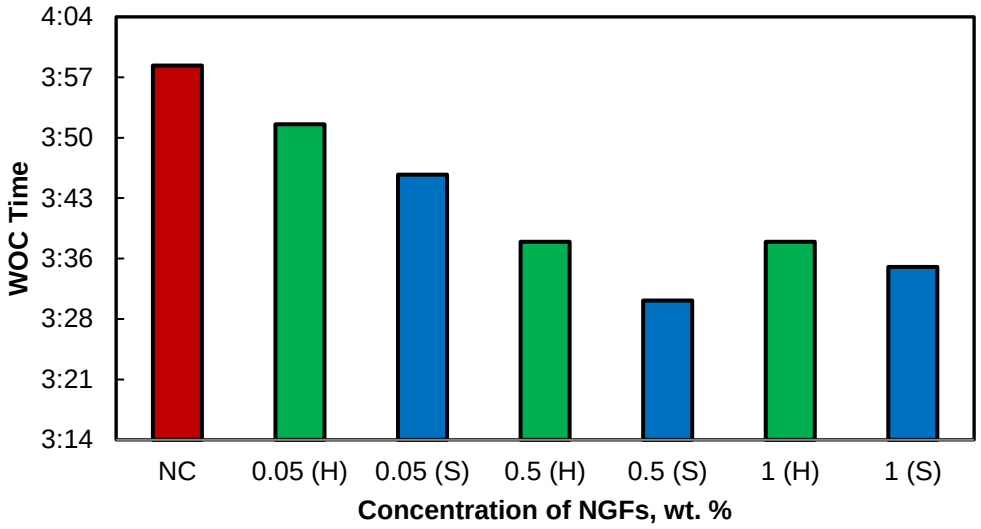


Figure 3.12: WOC of different NGFs based cements prepared by hand mixing (green) and sonication (blue) methods

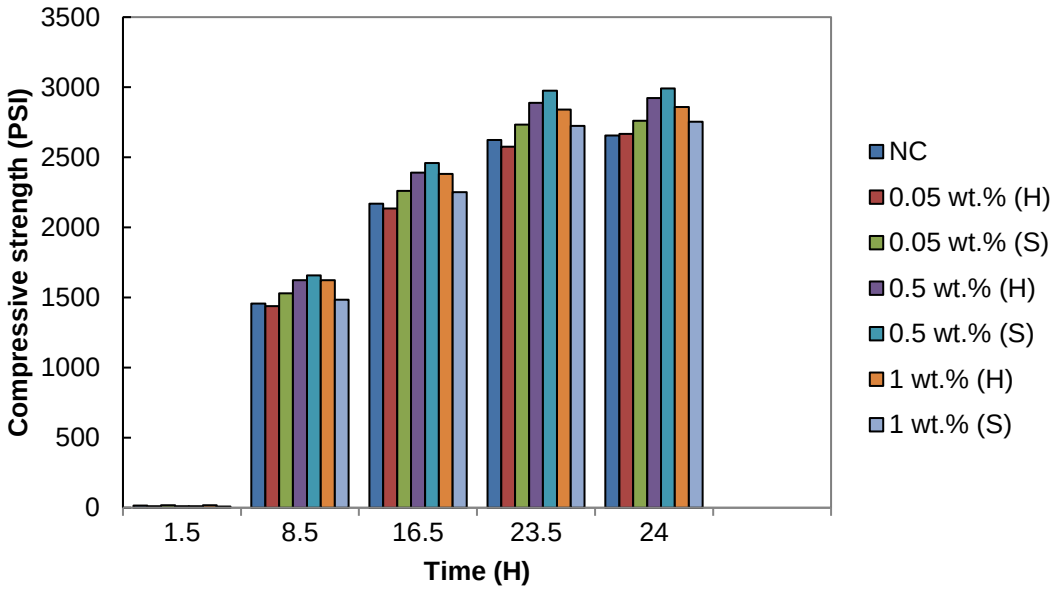
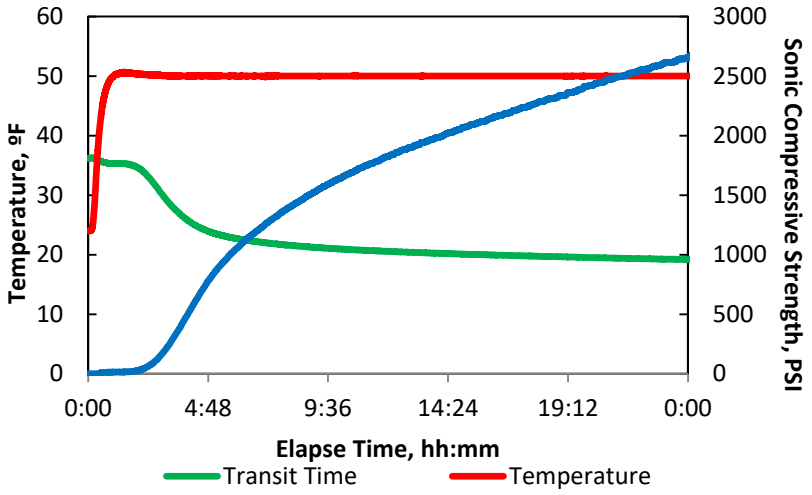
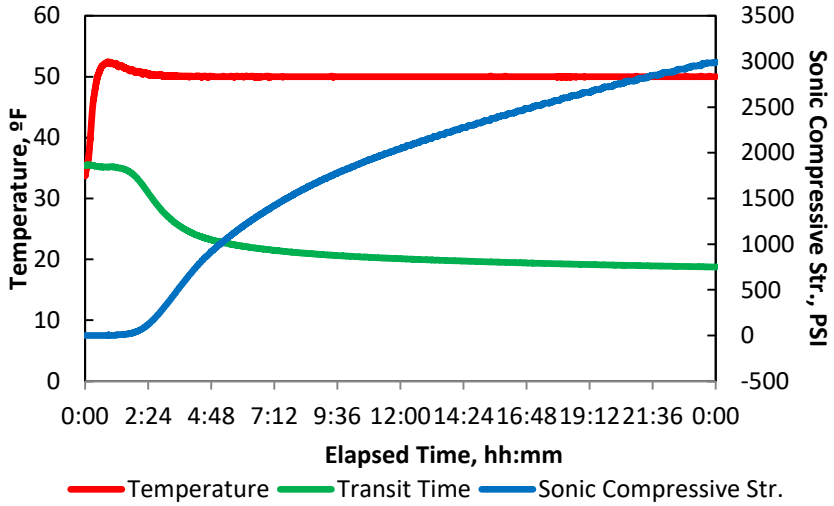


Figure 3.13: Compressive strength development of NGFs based cements prepared by the hand mixing (H) and sonication (S) methods

Neat Cement



0.50 wt.% NGFs (S)



1.00 wt.% NGFs (S)

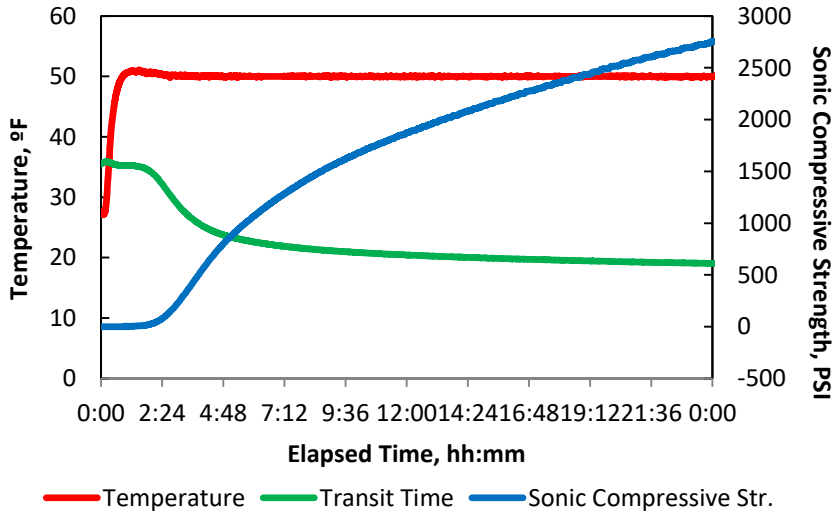


Figure 3.14: Strength development in the sonicated samples measured using the UCA

It was also found that after 24 hours, all the samples give a higher compressive strength than the neat cement, although the cement with 0.5 wt. % NGFs prepared through the sonication method had the highest strength with the value of close to 3000 PSI (21 MPa). Figure 3.15 shows the compressive strength of the neat cement, sonicated and hand-mixed samples obtained from the UCA.

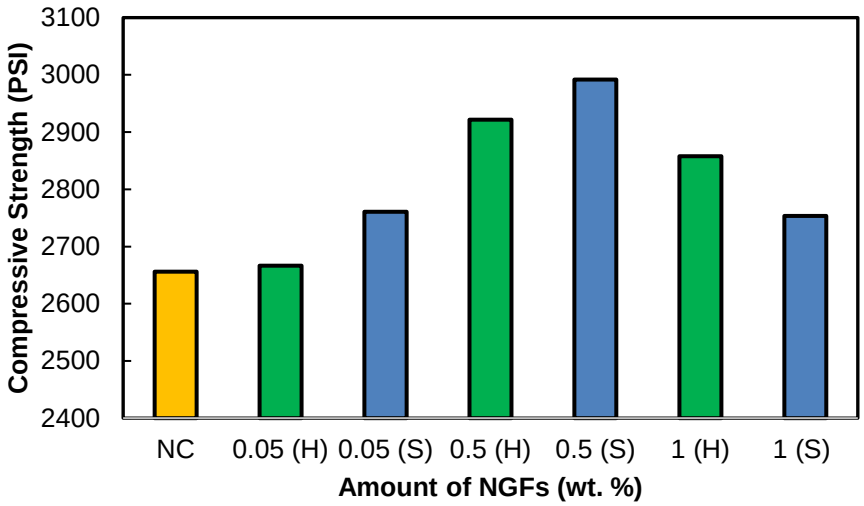


Figure 3.15: Compressive strength of the neat cement, hand-mixed (H) and sonicated (S) samples after 24 hours of curing in UCA

It should be noted that the compressive strength obtained from the UCA is a function of chemical reactions taking place between the cement, additives (nanoparticles) and water. However, NGFs are chemically inert and as such, they are unable to enhance the chemical reactions to improve the cement matrix structure. The improvement observed in the compressive strength can be linked to the physical structure of the cement which has been improved by a proper dispersion of NGFs. It appears that dispersing 0.5 wt. % NGFs into the cement matrix would give the best results in terms of the compressive strength. Any quantity greater than this threshold may reduce the reaction between portlandite and water, resulting in a poor hydration process. That could be the reason behind the lesser strength development of 1 wt.% NGFs cement compared to the one with 0.5 wt.% NGFs.

3.3.6.2. Destructive Test

A Uniaxial Testing Machine (UTM) with semi-automatic configurations was used in this study to determine the destructive compressive strength of the cement samples. Figure 3.16 shows the UTM machine and one of the samples used for destructive tests.

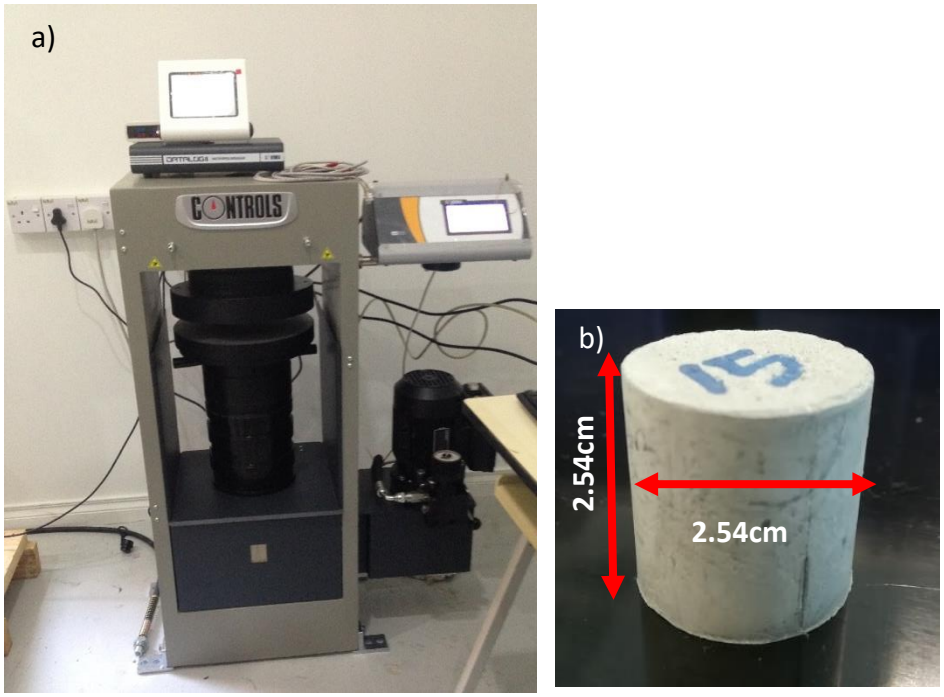


Figure 3.16: a) Uniaxial Compression Testing Machine and b) one of the tested cement samples

To prepare the samples, the cements were placed into a mould and fully immersed in the water bath at the temperature of 50^{o}C for 24 hours. The UTM machine was operated by the hydraulic transmission of loads where the axial stress could increase up to a defined level. To do the tests, the axial stress was increased constantly by the pressure-compensated proportional valve until the failure of the cement specimen. This procedure was repeated at least 3 times to ensure that the results obtained have sufficient accuracy. The compressive strength was then measured from the maximum force sustained before failure. In order to obtain the compressive strength, the forces recorded at failure were divided by the cross-sectional area of the samples which was 0.000507 m^2. The results obtained from running the destructive

compressive strength tests on the hand-mixed and sonicated NGFs cement samples are shown in Figure 3.17.

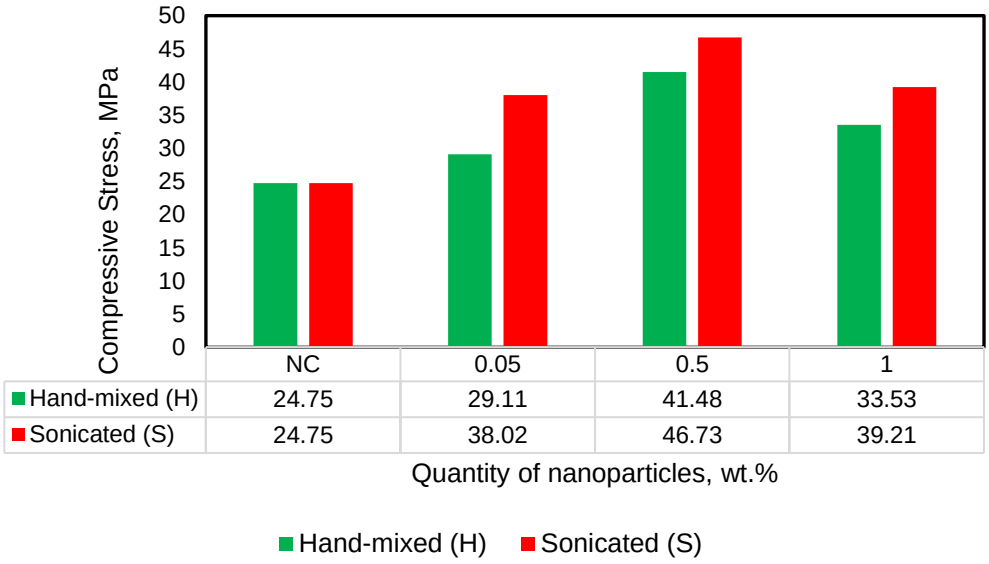


Figure 3.17: Compressive strength of the sonicated (S) and hand-mixed (H) cement samples

From Figure 3.16, it seems that the samples prepared through the hand mixing or sonication can provide a higher strength than the neat cement. It is believed that NGF can act as a filler and densify the cement structures by filling up the pores, which in turn increases the mechanical strength. This was the same conclusion made by Zuo et al. (2017) where they treated their cement mortar with 60-400 mesh glass flakes (GFs). The specimens were cured for 21 days in a dry-curing box and the result showed that adding 5-20 wt% GFs increases the compressive strength by densifying the concentre matrix and filling up the pore spaces.

Comparatively, the sonicated samples had a better performance compared to the manual-mixed sample where the sample with 0.5 wt.% NGFs had the highest strength. This could be due to the proper integration of NGFs with the cement matrix due to the dispersion as shown in Figure 3.17. In this figure, hand-mixed (H) samples were presented on the left, whereas sonicated (S) samples were displayed on the right. The results showed that the sonicated samples would have a denser texture while the amount of micropores seems to be more obvious in the hand mixing samples. Micropores and microfractures are the drawbacks that could manifest themselves in the compressive strengths (Zhao et al., 2014).

In fact, applying sonication gives a denser and smoother structure to the cement than can increase its strength against the load applied. It also appeared that when the concentration of NGFs goes above 0.5 wt.%, saturation threshold may reach and the compressive strength decreases due to the poor interaction between the NGFs and the cement matrix. The obtained result was then compared with the non-destructive ones as given in Table 3.12 and shown in Figure 3.18:

Table 3.12: Comparison between Non-destructive and Destructive Strengths of NGFs Based Cement after 24 hours

Type of NGFs Based Cement, wt.%	Non-Destructive Compressive Strength, MPa	Destructive Compressive Strength, MPa
0	18.31	24.75
0.05 (H)	18.38	29.11
0.05 (S)	19.04	38.02
0.5 (H)	20.14	41.48
0.5 (S)	20.63	45.73
1.0 (H)	19.70	33.53
1.0 (S)	18.98	39.21

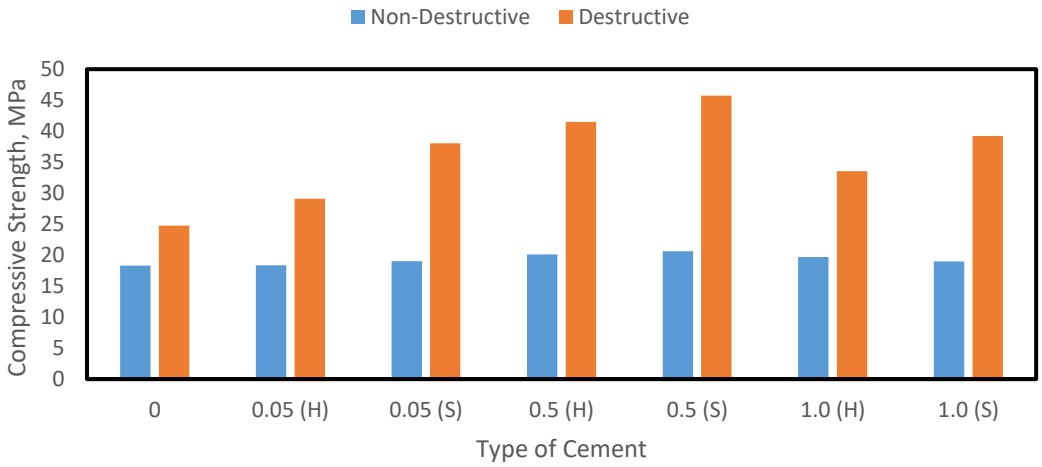


Figure 3.18: Comparison of the compressive strengths observed in different samples

3.3.6.3. Different Curing Ages

Given the fact that some of the cement samples were cured and exposed to the atmosphere for 28 days, attempts were made to evaluate the effect of the curing age on the performance of the cements modified by NGFs (Figure 3.19). Figure 3.20 compares the compressive strength of the sonicated samples with two different curing ages.

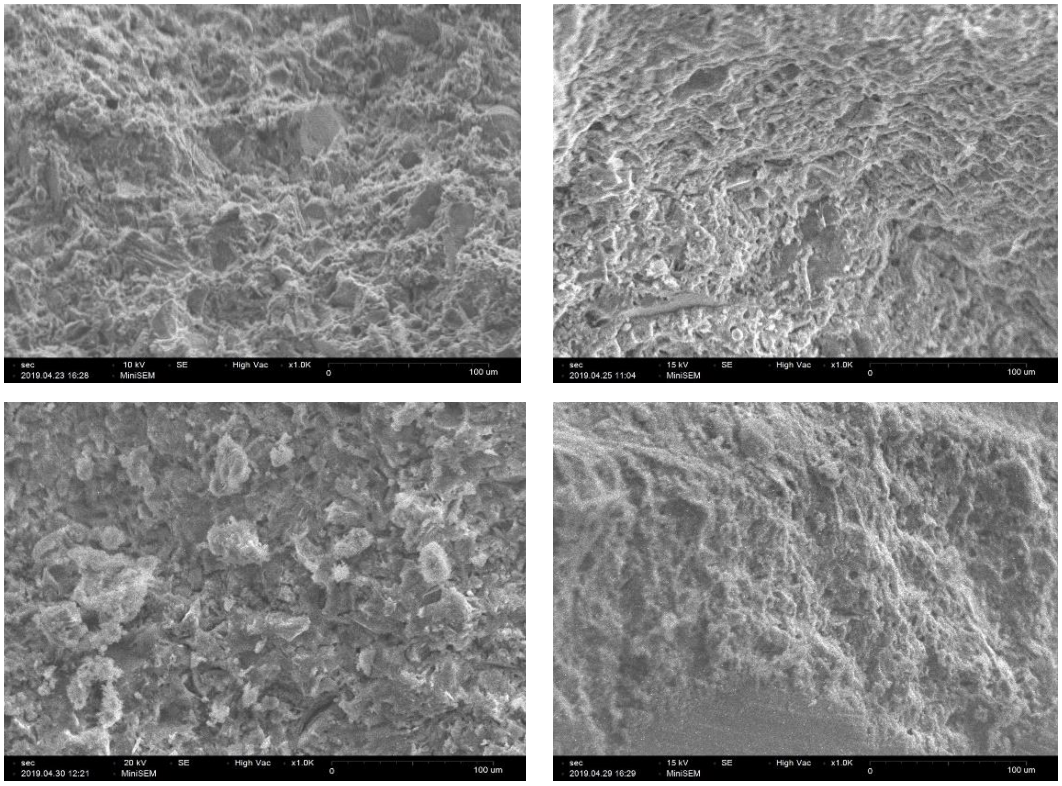


Figure 3.19: SEM images of the hand-mixed (left) and sonicated (right) samples with 0.5 wt% (top) and 1 wt.% (bottom) NGFs

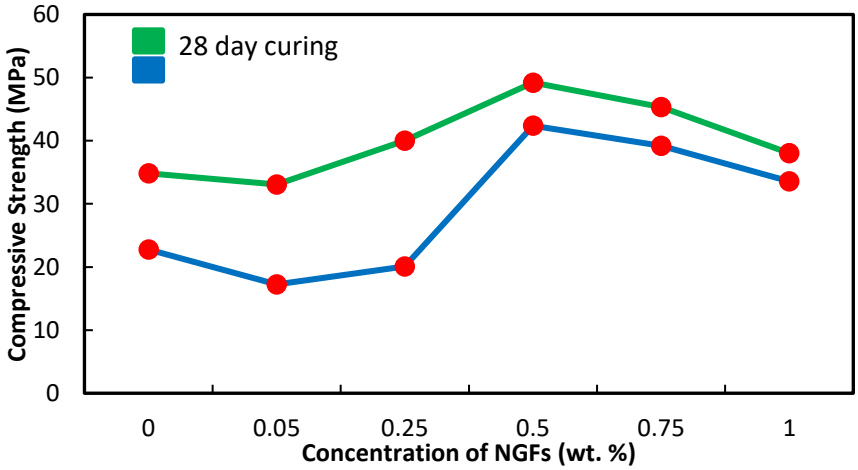


Figure 3.20: Compressive strength of the sonicated samples with NGFs cured for 1 and 28 days

The results obtained indicated that the highest compressive strength is obtained by the samples with 0.5 wt. % NGFs regardless of the curing period. However, the compressive strength was significantly reduced with the replacement ratio of lesser than 0.5 wt. % for the samples cured for one day. In fact, the neat cement had a higher compressive strength than the cements with 0.05 wt. % NGFs even after 28 days of curing. This could be because of the slower hydration reaction caused by the amount of the cement replaced. By increasing the amount of NGFs to 0.5 wt. %, the cement hydration is accelerated and as such a greater strength was achieved. The large surface area of the nanoparticles can increase the water absorption which favours the development of the cement hydration. Besides, NGFs are already used as a reinforcing filler in many industrial applications to improve the resistance against corrosion and mechanical failure (Nematollahi, et al, 2010; Ghadami, et al., 2014). According to these studies, NGFs can reinforce the cement mechanically by aligning themselves in a parallel structure, which results in a better durability. Nevertheless, there is a threshold value for the replacement of NGFs that should not be ignored. Once the replacement goes beyond 0.5 wt. %, the cement strength reduces. It is probable that an excessive amount of NGFs, even though they are well-dispersed, are overloaded to fill up the pore spaces between the cement particles. To further evaluate the impact of NGFs on the cement microstructure, X-ray diffraction analysis was carried out as discussed in the following sections.

3.3.7. X-Ray Diffraction (XRD) Analysis

X-Ray Diffraction (XRD) is one of the tests that can effectively define the state of the cement hydration. It is done by bombarding the cement powder at different angles where the presence of various crystalline phases in the cement matrix can be identified based on their unique reflected waveforms. The results obtained from this test is presented in the following subsections.

3.3.7.1. Optimum Quantity of NGFs

In this study, a total number 6 samples including neat cement (NC), and a range of 0.05 to 1 wt.% nano glass flakes (NGFs) samples, which are all prepared by the sonication method, were sent to University Teknologi Petronas UTP for the XRD test.

To interpret the results obtained, Match! Software provided by Crystal Impact was used. Figure 3.21 shows the results obtained from running the XRD tests on the samples.

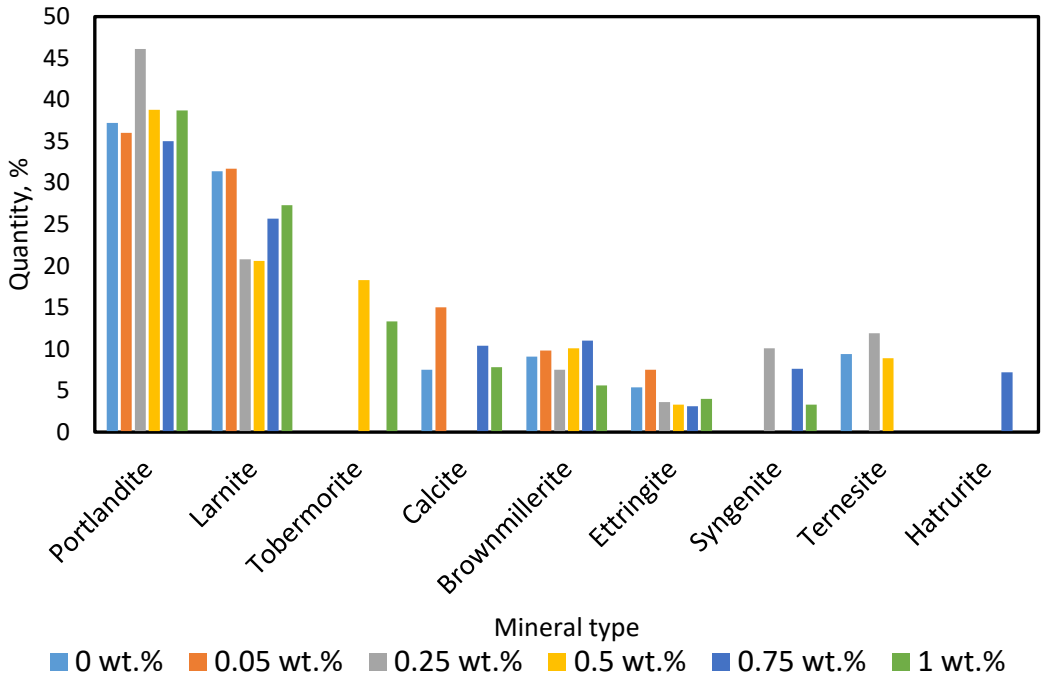


Figure 3.21: Different crystalline phases obtained from running the XRD tests on the sonicated cement samples modified by NGFs

The results obtained indicated that the main component of the neat cement, as expected, is portlandite, followed by larnite (belite), which is some sort of calcium silicate mineral. The presence of larnite can be attributed to the late strength development and low reactivity of the cement. Once reacted with water, larnite produces calcium silicate hydrates (C-S-H) and portlandite ($Ca(OH)_2$). Among all the samples, the cement with 0.25 wt.% NGFs had the highest amount of portlandite while the cement with 0.5 wt.% NGFs had the least amount of Portlandite in its structure, indicating the accelerated interactions posed by the NGFs in the cement during curing.

It should be noted that larnite indicates the severity of the interactions taking place in the cement and the amount of C-S-H produced. Comparatively, the sample with 0.75 wt.% NGFs had the lowest Portlandite but the amount of larnite in its structure

was higher than the sample with 0.5 wt. % NGFs. Thus, it was concluded that the lesser amount of portlandite in the sample with 0.75 wt.% NGFs could only be due to the replacement ratio, not the interaction posed by the NGFs.

There are some other crystalline phases included in the samples such as thermodynamical (controls the setting and hardening of the cement paste), Calcite (indicates cement hydration), and Brownmillerite (which is a representative of the strength development), but given their low percentage, no strong discussion could be provided to support the results obtained.

3.4. Discussion

Despite of the large surface areas, NGFs in the dry powder form have a strong van der Waals force, which can easily result in agglomeration. Hence, a proper dispersion method such as the one proposed in this study must be considered to breakdown the clusters of nanoparticles for an effective physical and mechanical improvement. It is also possible that the mixing of negatively charged NGFs with negatively charged cement could create repulsive forces among the particles and prevent agglomeration (Wang et al., 2014). Having said that, the results obtained from the sonicated (S) samples appear to be better than hand-mixed (H) samples. In addition, it was found that the optimum amount of NGFs that can be added to cement for the best performance is 0.5 wt.%. It would give an acceptable rheology, free water, and compressive strength development to the cement over time. It would also have the least amount of portlandite which is crucial to survive through an acidic environment.

3.5. Conclusions

In this study, two mixing methods were tested and their effects on the rheological and mechanical properties were examined. As an overview, among all, the optimum quantity of NGFs was found to be 0.5 wt.%, which gives the best compressive strength and acceptable rheological behaviour. The following conclusions were also made:

- It is crucial to disperse NGFs properly in order to gain a better rheology and strength.
- NGFs are electrokinetically stable in an alkaline environment.

- Presence of NGFs would increase the surface area of the cement particles and reduce the free fluid volume.
- In spite of the content or the mixing methods used, the compressive strength increases once the NGFs is added to the neat cement.
- Adding more than 0.5 wt.% NGFs to the cement reduces the strength development rate. This could be due to the poor interaction of NGFs with cement particles.

Chapter 4: Application of Multi-Walled Carbon Nanotubes (MWCNTs) in Well Cementing

4.1. Introduction

Cement is commonly characterized as a quasi-brittle material with a poor toughness and a low tensile strength. These features often lead to the development of cracks under the acidic or High-Pressure High-Temperature (HPHT) conditions (Bajare et al., 2012). To control the cracking in the cement, several effective methods such as reinforcement using fibres (e.g. nylon), natural cellulose (e.g. pulps) and inorganic fibres (e.g. glass) have been proposed with some success and failure under different circumstances (Musso et al., 2009).

Carbon NanoTubes (CNTs) have established a huge interest in the past few years which is mainly because of their extremely high mechanical, thermal and electrical properties. It is believed that CNTs can prevent the development of cracks and enhance the strength properties of different materials if properly integrated in their matrix (Leonavičius et al., 2017). CNTs are structurally rolled graphite sheets commonly produced in a single-walled (SWCNTs), double-walled (DWCNTs) or multiple-walled (MWCNTs) forms with the diameter of 1-2nm (Ibrahim, 2013). Due to their size and large surface areas, CNTs pose unique physical, chemical and mechanical characteristics which make them a great candidate for many commercial applications such as filling agents (Saeed and Khan, 2016), efficient gas adsorbents for environmental conservation (Ngoy et al., 2014) and supporting media for inorganic and organic catalysts (Mabena et al., 2011). Having said that, Cwrizen et al. (2009) used CNTs in the cement design and reported 50% increase in the compressive strength when 0.05% - 0.15 wt.% of CNTs were added to the cement while Yakovlev et al. (2006) reported a 70% increase in the compressive strength of the concrete when 0.05 wt% of CNTs was applied. They concluded that changes in the morphology of the cement induced by CNTs can improve the mechanical strength of the cement but an optimum amount of CNTs must be used to achieve the best results.

In this chapter, attempts are made to investigate the effect of MWCNTs on the physical, rheological and mechanical properties of Class G cement and determine the optimum amount of CNTs that can give the best performance to the conventional class G cement.

4.2. Methodology

4.2.1. Cement Composition

For this study, MWCNTs was used for the modification of class G cement. UG Plus 101 PD MWCNTs was bought from Ugent Tech Sdn Bhd. The properties of MWCNTs are GIVEN in Table 4.1.

Table 4.1: The properties of MWCNTs used for this research

Chemical Compositions	
Carbon nanotubes	> 98%
Amorphous carbon	< 1
Nickel oxide	< 1%
Material Properties	
Physical Appearance	Powder form, black colour, odourless
Density, g/cm^3	~2.1
Surface Area, m^2/g	250 - 300
Diameter, nm	10 - 30
Length, µm	5 - 20
Electrical Conductivity, S/m	1 x 10^5
Melting Point, °C	3652 - 3697

Preparation of the cement slurry was according to the API standard practice 10A, which is one of the most common standards used in the industry. This recommended practice was also followed to measure the fluid loss, rheology and compressive strength of the cement samples. However, there was no standard for adding MWCNT to the cement and determine its optimum quantity to achieve the best performance. Thus, a mixing procedure was proposed and a complete set of tests was done on the nanomodified cement samples to ensure that they can provide the functionality

needed. Figure 4.1 shows the MWCNs used together with the cement sample modified by them.

Figure 4.1: left) MWCNTs used in this study; right) The cement sample modified by MWCNTs

4.2.2. Mixing Techniques

To prepare the cement samples, neat cement (i.e. the cement without any additives) was mixed with deionised water according to the API Standard 10-A (2005), with a water to cement (w/c) ratio of 0.44. This ratio was kept constant once MWCNTs were added to the cement. Two mixing methods were considered for the cement slurry preparation including manual/hand mixing and ultrasonication which are discussed in the next section.

4.2.2.1. Manual/Hand Mixing Method

In the hand mixing method, MWCNTs were directly added to the cement and hand-mixed constantly for 5 minutes. The slurry was then mixed by the Fann Constant Speed Mixer (Figure 4.2 left), at the speed of 4000 rpm for 15 seconds, followed by a high-speed mixing at 12,000 rpm for 35 seconds. This approach in this study is referred to as the conventional mixing or manual mixing method.

4.2.2.2. Altered Method (Sonication)

In this section, the neat cement was mixed with deionised water according to the API Standard 10-A (2005) with a water to cement (w/c) ratio of 0.44. This ratio was kept constant when MWCNTs were added to the cement. Before mixing, MWCNTs was added to the deionized water and subjected to ultrasonication for a better dispersion and prevention of agglomeration. This dispersion was done with the help of LSP-500

Ultrasonic Processor. It should be noted that nanoparticles have a large surface area and can naturally agglomerate. In addition, MWCNTs are hydrophilic, which means that they flocculate easily once exposed to water. To resolve these issues, ultrasonication was done for 15 minutes to ensure that a proper dispersion would take place. Due to the heat generation, water evaporation was determined and compensated prior to the next stage.

Preparation of the cement slurry was done using Fann Constant Speed Mixer where the samples were mixed at the speed of 4000 rpm for 15 seconds followed by a high-speed mixing at 12,000 rpm for 35 seconds. A total number of 5 samples were prepared at the end with the ratios reported in Table 4.2. Figure 4.3 shows the flowchart of the steps taken to prepare the cement samples.

According to Chan and Andrewes, (2010), 0.25 wt% MWCNTs is an optimum quantity that can be added to the cement for the best performance while others suggested that much lesser amount, i.e. 0.08%, must be used to avoid unfavourable rheological properties (Jang et al., 2016). In this study, however, different quantities of CNTs were added to the cement and their impact on the cement performance were examined through a series of Zeta potential, density, free fluid, compressive strength, and rheological tests. The workflow of the overall methodology is shown in Figure 4.4.

Table 4.2: Ratio of water, cement and CNTs used for the purpose of this study

Sample No.	Percentage of MWCNTs (wt.%)	Weight of MWCNTs (g)	Weight of Cement (g)	Weight of Deionised Water (g)
1	0	0	592	260.48
2	0.025	0.148	591.852	260.48
3	0.05	0.296	591.704	260.48
4	0.075	0.444	591.556	260.48
5	0.1	0.592	591.408	260.48
6	0.25	1.48	590.52	260.48

Figure 4.2: left) Fann constant speed mixer, and right) Fann Viscometer used in this study

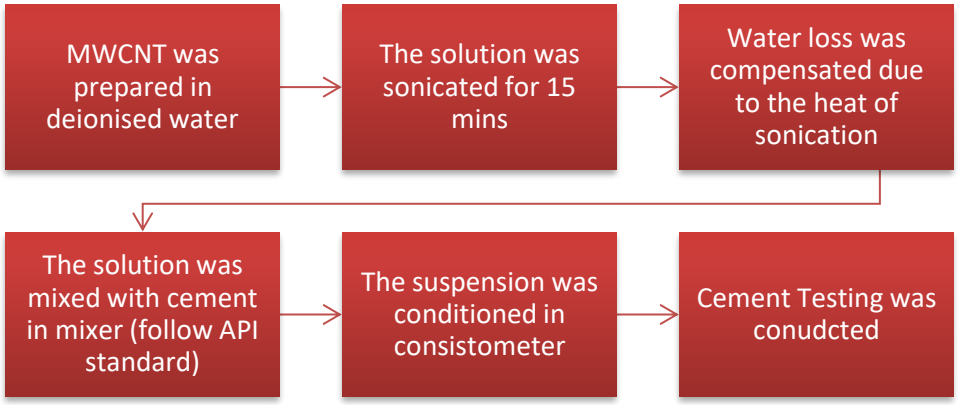


Figure 4.3: Flow chart of the cement preparation process through sonication

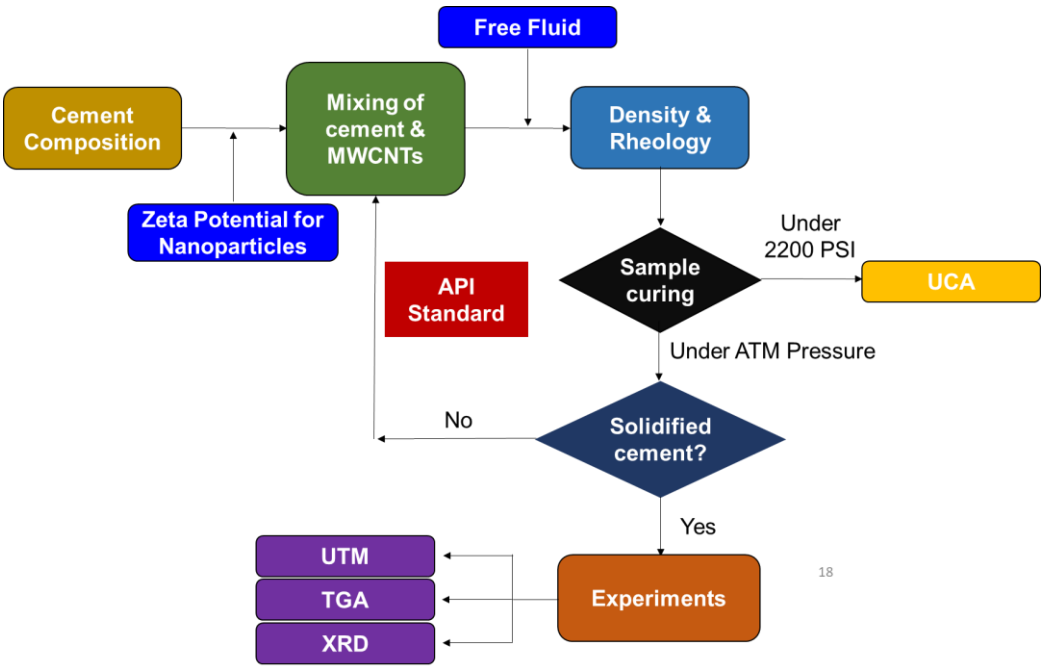


Figure: 4.4 Methodological workflow to design a MWCNTs-based cement

4.3. Experimental Results

4.3.1. Zeta Potential

To evaluate the surface charge of MWCNTs, zeta potential of different nanoparticle solution was measured under different pH by the help of Malvern Zetasizer ZS. This was done by adding HCl (0.5%) and NaOH (0.5%) to the dispersed solution and adjusting the pH values within the range of 1–13. The zeta potential was measured by the potential difference between the dispersion medium and the layer of the fluid attached to the dispersed particle. The magnitude of this potential difference indicates the degree of electrostatic repulsion of the charged particles in the dispersion. The results obtained from are shown in Figure 4.5.

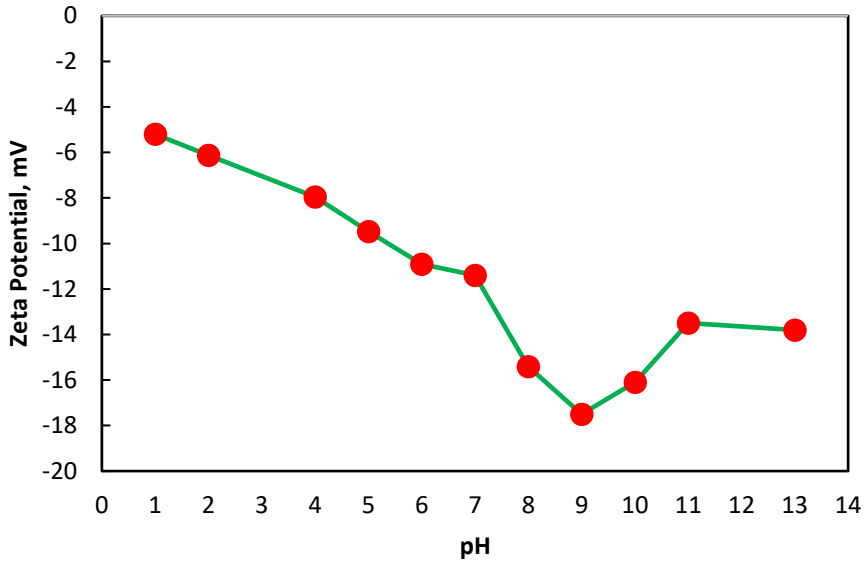


Figure 4.5: Variations of Zeta potential under different pH conditions for the MWCNTs dispersed solutions

The results obtained indicated that the negatively charged MWCNTs are much stable at the pH of 8-10 while MWCNTS would lose its surface charges when the environment becomes acidic. According to, Leonaviius et al., (2017), ultrasonic treatment can activate water and destroy the hydrogen bonds which may increase the pH and help to have an alkaline environment. This would create a favourable condition to have a stable nanofluid solution. It should be noted that a higher magnitude of zeta potential indicates a better stability to resist aggregation. This is mainly because at low magnitudes (negative or positive), the attractive force

between particles may overcome on the repulsive force, resulting in aggregation and electrical instability.

4.3.2. Density

Density is a crucial parameter of the cement to evaluate its static stability and ensure that the column of the cement placed in the annulus space will not cause any integrity issues (Lavrov and Torsaeter, 2016). It should be noted that MWCNT has a high aspect ratio, low bulk density and a large specific area (Yakovlev et al., 2006). Thus, adding MWCNTs gives an efficient and uniform matrices structure to the cement. In this study, the weight of the cement slurries was measured using the FAN pressurized mud balance with the result shown in Figure 4.6.

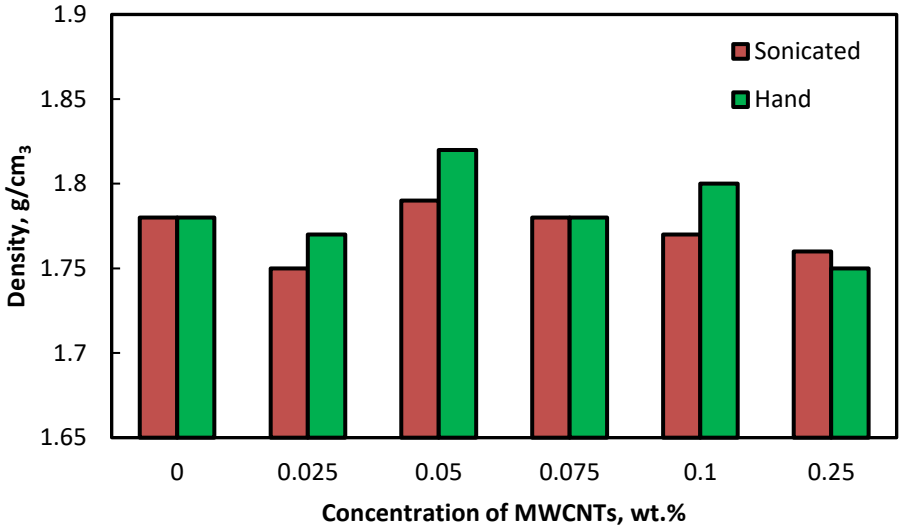


Figure 4.6: Density of the cement slurries prepared by different mixing methods versus their MWCNTs content

The results obtained indicated that the density of the cement samples is not significantly affected by MWCNTs. The changes made are within the range of 1.75 g/cm^3 – 1.8 g/cm^3. Thus, quantity of MWCNTs is not a major factor influencing the density of the cement once property dispersed. There are, however, some minor differences between the density of the sonicated and hand-mixed samples which could be linked to the uncertainty induced by reading the values of the mud balance given the fact it is not a digital apparatus.

4.3.3. Free Fluid Test

The free fluid test was carried out according to the API standard 10-A. To do the test, the cement samples were conditioned after preparation using an atmospheric Consistometer at the temperature of 27^{o}C for 20 min. The cement was then transferred into a dry 500ml conical flask, sealed and put aside on a free vibration surface for 2 hours (see Figure 4.7). Subsequently, the volume of supernatant fluid (V_{ff}) was removed from the conical flask with the help of a syringe and measured by the accuracy of ±0.1 ml. With the help of the following equation, the percentage of free fluid (%ff) was then calculated:

$$\%ff = \frac{V_{ff} \times \rho}{m_s} \times 100 \qquad (4.1)$$

where Vff is the volume of the free fluid collected from the conical flask, p is the density of the cement and m_s is the mass of the cement. The results obtained are given in Table 4.3 and shown in Figure 4.8 for different cement samples.

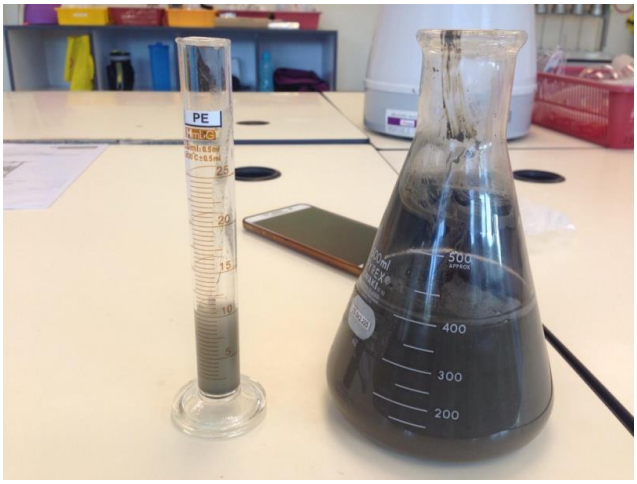


Figure 4.7: Accumulation of free fluid on the top of the cement slurry in the free fluid test

Looking at Table 4.3, it appears that as the quantity of MWCNTs increases in the cement slurry, the volume of free fluid decreases. This shows that the water adsorption improves with the presence of MWCNTs. Nevertheless, all the cement samples passed the threshold limit of the API standard and had the free fluid of less than 5.90%.

Table 4.3: Free fluid of different cement samples

Percent of MWCNTs, wt. %	Weight of MWCNTs, g	Mass Transferred, g	Density, g/cm^3	Volume of free fluid, ml	Free fluid, %
0	0	765.10	1.78	11.50	2.68
0.025	0.153	763.80	1.75	11.30	2.59
0.050	0.296	766.04	1.79	10.50	2.45
0.075	0.444	765.47	1.78	9.50	2.21
0.10	0.592	763.80	1.80	8.70	2.05

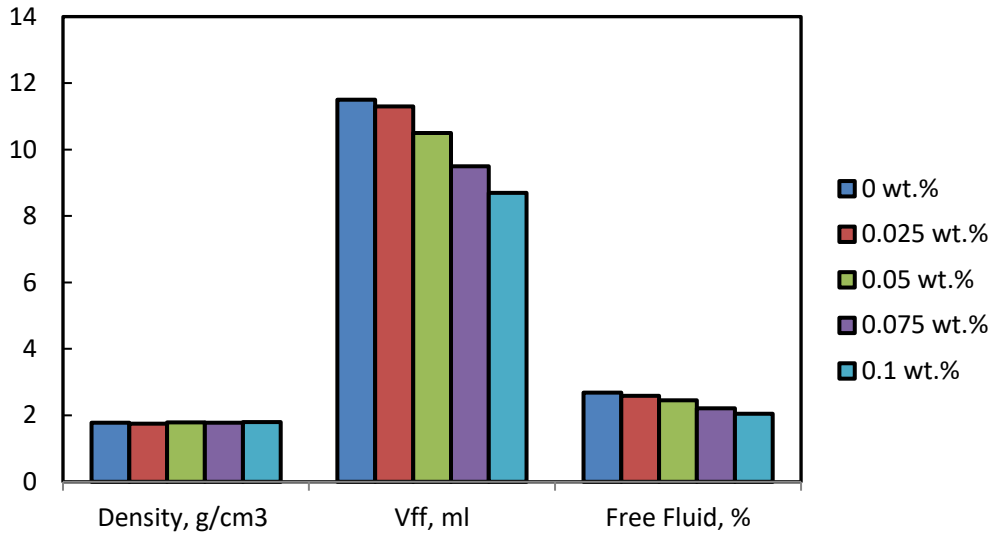


Figure 4.8: Density, volume and percentage of free fluid in the cement sample with different percentage of MWCNTs

4.3.4. Rheological Properties

As an integrated part of the cement design, characterization of the rheological parameters is important to determine the frictional pressure loss and pump horsepower. As it was mentioned earlier, there are two mathematical models commonly used in the industry to characterize the rheological behaviours of the cement which are known as the Bingham plastic and power law (Nelson, 1990). The Bingham plastic is presented by the plastic viscosity and yield point parameters while the power law is expressed by the consistently index, k, and behaviour index, n, in a shear rate-shear stress plot.

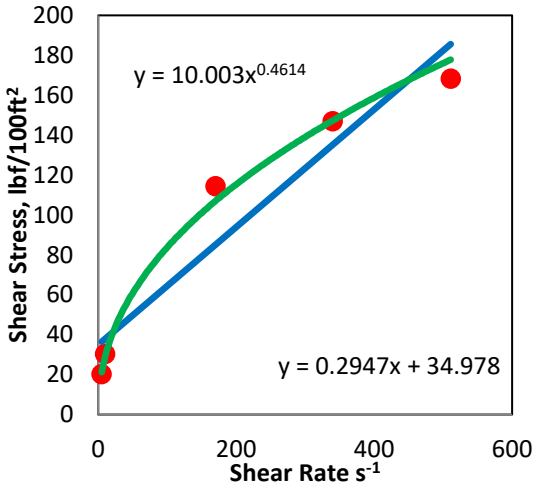
In this study, the rheology of the MWCNT cement composites was measured using the rotational viscometer. Prior to the test, the cement slurry was conditioned using the Fann Atmospheric Consistometer for 30 minutes at the temperature of 50^{o}C as per the API Standard 10-B (2013) recommendation practice. The slurry was then poured into the viscometer cup and the readings were taken at different speeds (i.e. 3, 6, 100, 200, 300 rpm), except 600 rpm. The strain rate versus strain stress plots were then used to determine the rheological parameters. The results obtained for the sonicated samples are shown in Figure 4.9 and given in Table 4.4 while the rheological parameters of the manual mixing samples are shown in Figure 4.11 and Table 4.5.

The results obtained indicated that the plastic viscosity consistently increases as the concentration of MWNTs increases. It seems that a small amount of MWCNTs (e.g., 0.025 or 0.05 wt.%) does not significantly change the viscosity while adding 0.075 to 0.25 wt.% MWCNTs may increase the viscosity by as much as 67%. It should be remembered that if the cement is too viscous (Se Figure 4.10), the frictional resistance of the cement against the flow causes difficulty during placement. As such, it is not recommended to add 0.25 wt.% MWCNTs or any higher concentration to the cement as it might drastically affect the whole cementing and the completion operation.

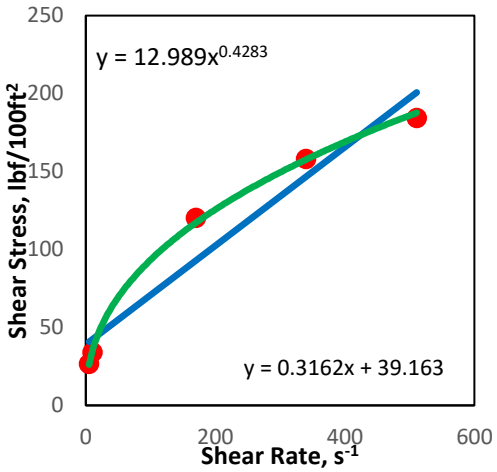
Table 4.4: Plastic viscosity and yield stress obtained from different sonicated MWCNTs contents

Sample No.	MWCNTs Content, %	Plastic Viscosity, cP	Yield Stress, lb/100ft^2	K, lbf.s^n/ft^2	n
1	0	141.17	35.84	0.1000	0.4614
2	0.025	151.70	39.16	0.1299	0.4283
3	0.05	156.70	35.42	0.1098	0.4567
4	0.075	176.50	37.93	0.0894	0.5141
5	0.1	217.8	48.85	0.1435	0.468
6	0.25	234.70	56.98	0.1898	0.4342

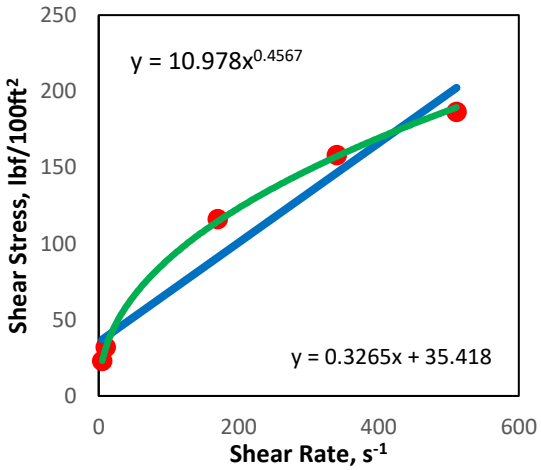
Neat Cement (NC)



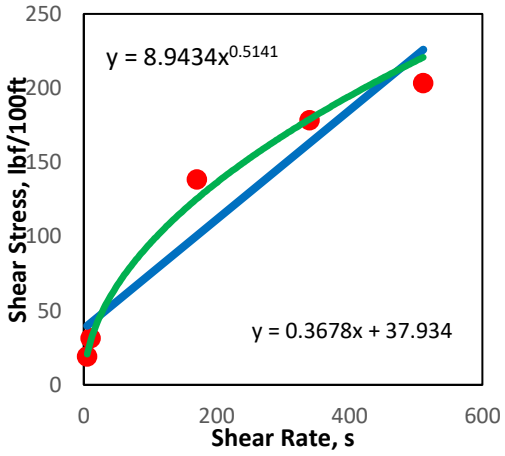
0.025 wt.%



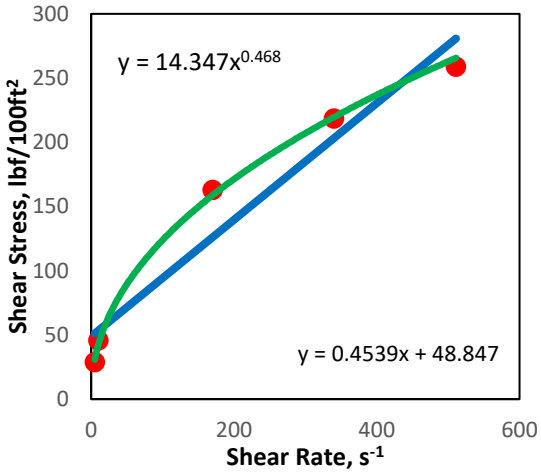
0.05 wt.%



0.075 wt.%



0.1 wt.%



0.25 wt.%

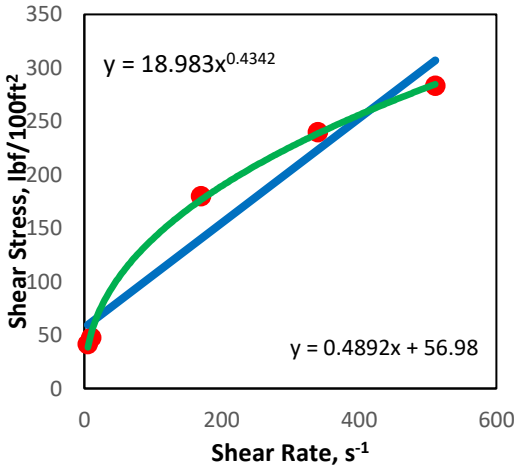


Figure 4.9: Shear stress versus shear rate plots obtained for the sonicated samples

Figure 4.10: The slurry condition of 0.25% cement replaced with MWCNTs

Looking at the results presented in Table 4.3, it also appeared that increasing the amount of MWCNTs from 0.025 to 0.1 wt.% has a minor impact on the yield stress. However, an excessive amount of MWCNTs may increase the chance of agglomeration and enhance the attractive potential of the particle's reaction. In fact, the cement sample with 0.25 wt.% MWCNTs was so thick and could not be considered for the cementing operation (see Figure 4.9). Thus, it was eliminated form further testing in the later stages.

Table 4.5: Plastic viscosity and yield stress obtained for the manual-mixed cement samples

Sample No.	MWCNTs Content, %	Plastic Viscosity, cP	Yield Stress, lb/100ft^2	K, lbf.s^n/ft^2	n
1	0	141.17	35.84	0.1000	0.4614
2	0.025	143.30	42.35	0.1523	0.3976
3	0.05	150.30	41.88	0.1450	0.4113
4	0.075	152.20	37.01	0.1024	0.4699
5	0.1	197.50	46.95	0.1233	0.4822
6	0.25	220.90	50.17	0.9514	0.5469

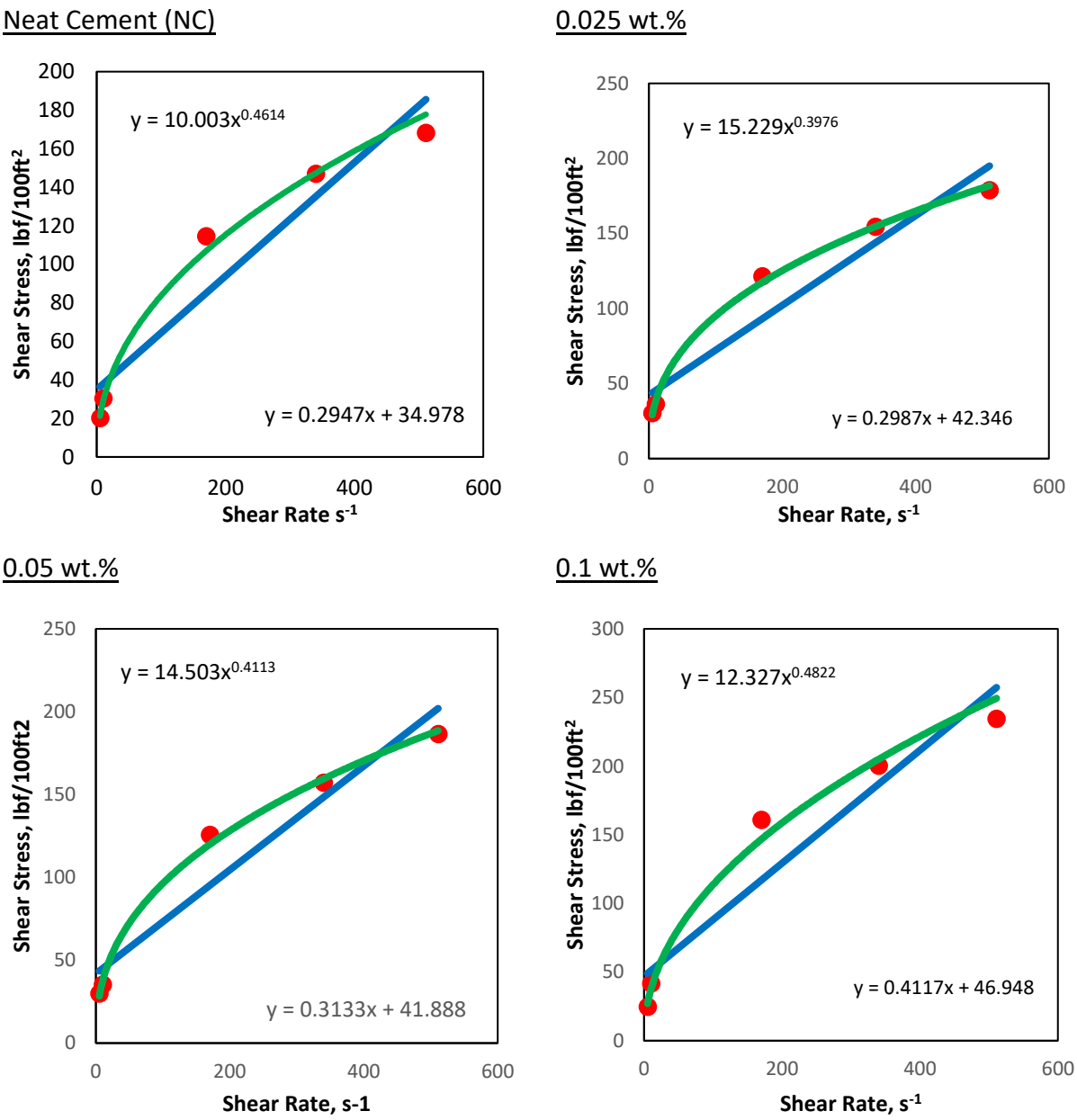


Figure 4.11: Shear stress vs shear rate plots for the manual-mixed samples

It was revealed that regardless of the mixing techniques, when the quantity of MWCNTs increases, the viscosity increases. Both 0.25 wt.% samples are having the highest viscosities, which are around 220.9 cp - 234.7 cp respectively for the sonicated and hand-mixing methods. However, generally, the sonicated samples had a greater plastic viscosity compared to the hand-mixed samples. This could be due to the loss of water during sonication which could not be compensated. In fact, although the water loss was compensated after the sonication process, the high temperature still accelerates the cement hydration and affect the viscosity (Hielscher, 2005;

Golaszewski and Cygan, 2009). Figure 4.12 compares the plastic viscosity and the yield point of the samples prepared by two different mixing methods.

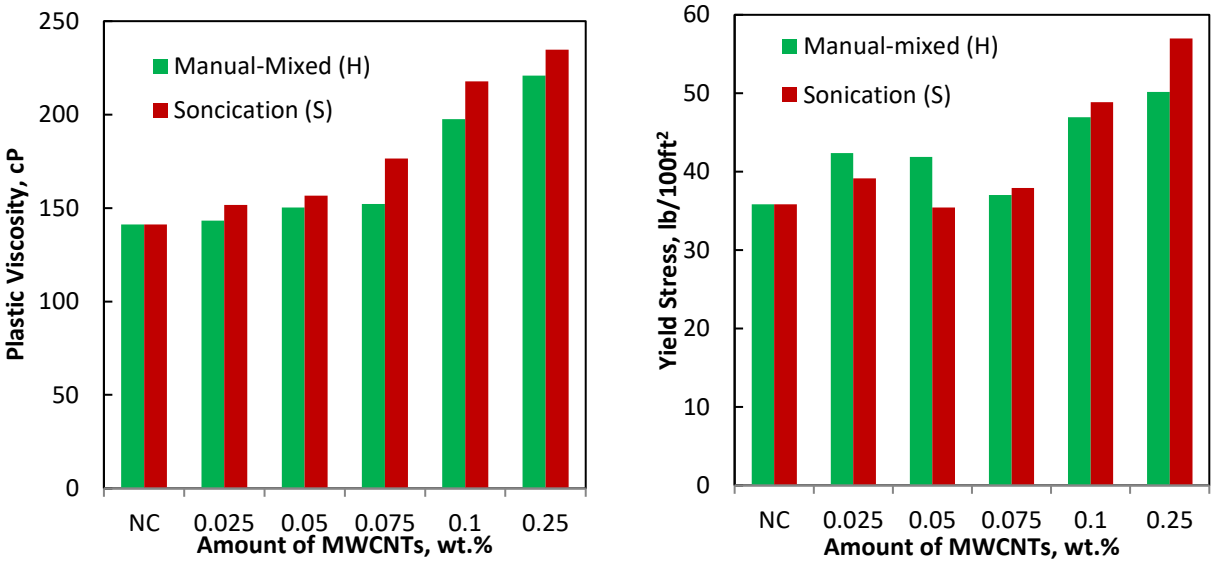


Figure 4.12: Plastic viscosity (left) and yield stress (right) comparison between the manual-mixing and sonicated samples

It should be noted that the results obtained from the yield stress is different from that of the plastic viscosity mainly because it is a function of the particle density of the cement component. According to Yim et al (2016), the particle distribution is a crucial factor and can significantly change the yield stress under different conditions. On the other hand, the viscosity is affected by both cement and nanoparticles, which makes it a function of the volume of solid particles and their packing density within the paste (Mbasha et al. 2015). Thus, changes in the viscosity would not necessarily affect the yield stress, if the cement particles are not well distributed. This verifies the fact that a proper dispersion method should be employed in order to get a consistent rheological behaviour for the nano based cements.

4.3.5. Thermogravimetric Analysis (TGA)

TGA analysis was also done to evaluate the amount of portlandite left in the samples prepared by different mixing methods. The test set-up and the procedure were the same as the ones explained earlier in the previous chapter.

4.3.5.1. Different Mixing Methods

Two mixing methods, the hand mixing (H) and sonication (S), were used to prepare the cement samples with 0.025 wt.% MWCNTs. The samples were cured in a water bath where the temperature was maintained at 50^{o}C. The results obtained were presented in Table 4.6.

Table 4.6: Weight loss and the amount of portlandite left in the cement samples with 0.025 wt.% MWCNTs prepared by two different mixing methods

MWCNTs Content, wt. %	0	0.025 (H)	0.025 (S)
Weight Loss, %	4.50	3.83	2.36
Portlandite, %	18.51	15.76	9.72

The results obtained indicated that the neat cement has the highest weight loss of close to 4.5% while adding MWCNTs even by 0.025 wt% could decrease the amount of portlandite due to the intuition of the pozzolanic reactions. Comparing the results of the samples, it was observed that the sonicated (S) sample has a lower weight loss compared to the conventional hand mixed (H) samples. According to Brandl et al. (2010), reduction in the amount of Portlandite would improve the performance of the cement when it is exposed to CO_2. It also appeared that the sonication method can properly disperse the nanoparticles in the cement matrix and as such the pozzolanic reaction reduces the amount of Portlandite produced by the end of the curing period.

4.3.5.2. Different MWCNTs Quantity

To evaluate the impact of MWCNT quantity on the cement hydration, two cement samples with 0.025 wt.% and 0.1 wt.% MWCNTs prepared by the same mixing method were chosen and compared. The results obtained are shown in Figures 4.13.

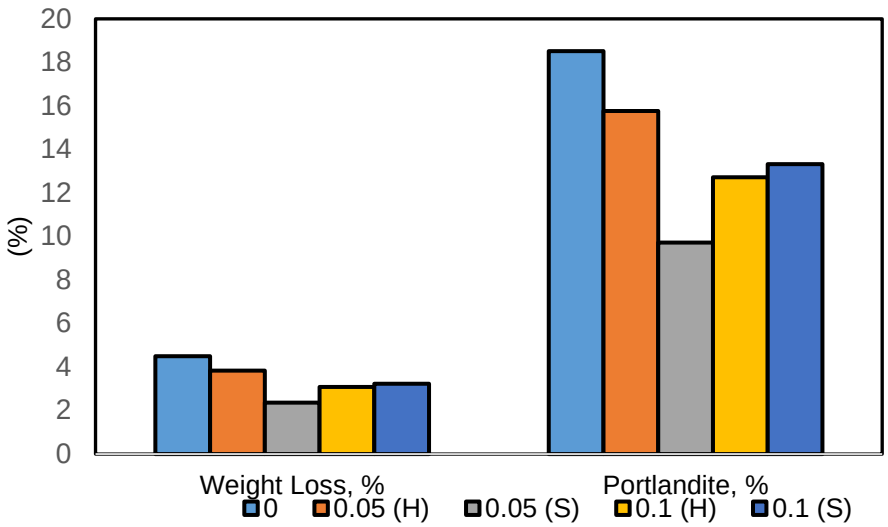


Figure 4.13: Weight loss and portlandite left in the samples with different mixing methods

The results obtained revealed that the least amount of portlandite left in the samples still belongs to the cement sonicated with 0.025 wt.% MWCNTs. Nevertheless, all the nano-modified cements had a lower Portlandite quantity compared to the neat cement due to the pozzolanic reactions taking place in the presence of MWCNTs. However, as the quantity of MWCNTs increases, agglomerates can be easily initiated and as such the interactions with the cement particles decreases (Korayem et al., 2017). As a result, water would chemically react with cement and produces more Portlandite.

4.3.5.3. Different Curing Conditions

To study the effect of the pressure and temperature on the cement hydration, the samples with 0.025 wt.% and 0.1 wt.% MWCNTs were chosen. In this stage, only the sonicated samples were considered given their better overall performance. The samples were examined under two different conditions of: 1) exposure to the temperature of 50°C and the pressure of ~16MPa (UCA sample); 2) exposure to the temperature of 50°C and atmospheric pressure (water bath sample). The result obtained from this analysis is presented in Figure 4.14 and Table 4.7. It was observed that the samples cured under the UCA condition have a higher mass loss than those cured under the water bath condition. This outcome is opposing with the NGFs one,

whereby their mass loss is relatively lower under the high pressure condition. Sedaghatdoost et al. (2019) claimed that the high surface area of MWCNTs would increase the water absorption rate, producing more cement products, resulting in a higher mass loss. Hence, under higher pressure, more water could be absorbed and the portlandite production could be enhanced. In addition, all MWCNTs based cements have lesser mass loss compared to the control sample. It is possible that the MWCNTs particles filled up the pores in the cement matrix, made the MWCNTs containing samples denser. Based on the study of Khalid and Waheed (2017), denser cementitious materials would display a lower mass loss.

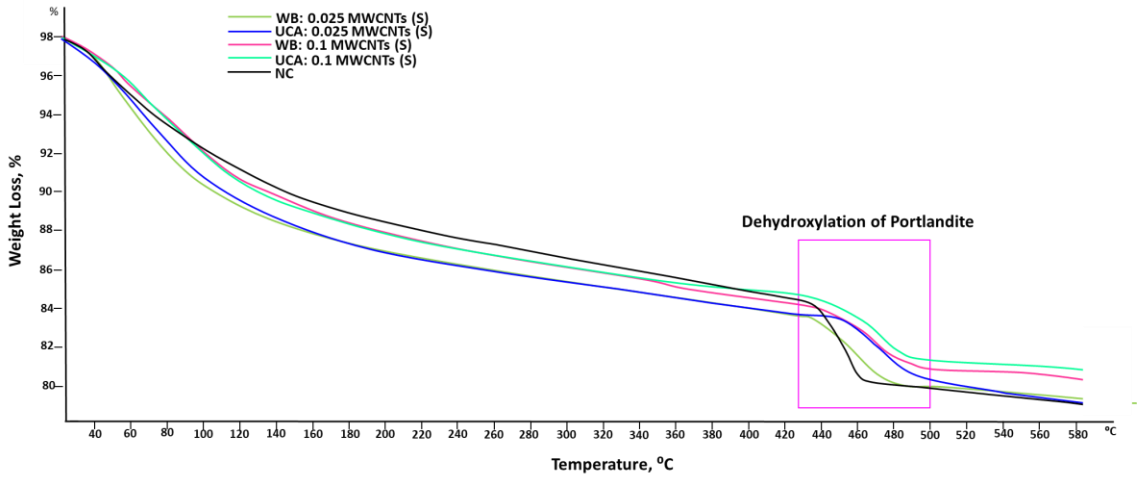


Figure 4.14: TGA plot of 0.025 and 0.1 wt.% of MWCNTs based cement samples with different curing conditions.

Table 4.7: TGA results of the sonicated MWCNTs based cements with different curing conditions

Sample No.	MWCNTs, wt.%	Curing Condition	Weight Loss, %	Portlandite, %
1	0	water bath	4.50	18.51
2	0.025	water bath	3.83	15.76
3	0.025	UCA	4.13	17.00
4	0.1	water bath	3.24	13.32
5	0.1	UCA	3.35	13.77

4.3.6. Destructive Compressive Strength

Compressive strength was another property of the cement that was determined to examine the effect of adding MWCNTs into the cement. To determine this property, the Control Groups Semi-Automatic EN Tester was used. To prepare the specimen for the test, the cement samples were placed into a cylindrical mould and fully immersed in the water bath with the temperature of 50^{o}C for 24 hours. Upon curing, the samples were placed into the machine and the hydraulic load with the rate of 18 MPa/Min was applied on them. The results obtained are presented in the following subsections.

4.3.6.1. Different Mixing Methods

In this stage, the cement samples were prepared using the two mixing methods and tested for their strength. Both sets of the samples were cured for 28 days and the results were compared in Table 4.8 and Figure 4.15.

The results obtained indicated that regardless of the mixing methods, the samples with 0.025 wt.% MWCNTs had the highest compressive strength. It appears that as the quantity of MWCNTs increases in the cement, the compressive strength increases. However, once the quantity of nanoparticles exceeds 0.075 wt.%, the development of the compressive strength is negatively affected. Comparing the mixing methods, the sonicated samples had a relatively higher cement strength. This could be due to the integration of nano and the cement particles posed by the sonication approach. Hence, a proper dispersion is essential to ensure that MWCNTs will improve the cement performance.

Table 4.8: Compressive strength obtained from the samples with different mixing methods

Sample No.	MWCNTs Content, wt.%	Compressive Strength, MPa (H)	Compressive Strength, MPa (S)
1	0	34.85	34.85
2	0.025	41.98	47.92
3	0.05	44.45	51.88
4	0.075	43.86	45.74
5	0.1	42.28	43.17

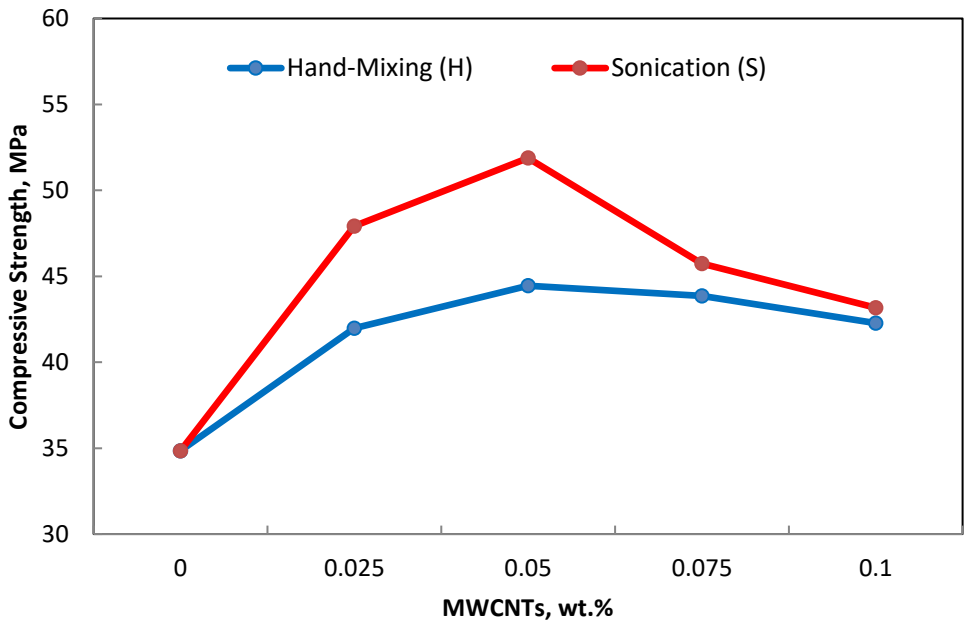


Figure 4.15: Compressive strength of the sonicated samples with different mixing methods

4.3.6.2. Different Curing Periods

To study the influence of the curing period on the cement strength development, the samples were cured for 1 day and 28 days. The curing was done using the water bath under the temperature of 50 ^{o}C as it was mentioned earlier. The results obtained are shown in Figure 4.16 and summarised in Table 4.9.

It seems that after 1 of day curing, the compressive strength of the samples increases as the quantity of MWCNTs increases. This might be related to the development of the calcium hydrate silicates (C-H-S) in the cement matrix. In fact, it appears that a nanodispersed modifier, such as MWCNTs, would enhance the kinetics of the interaction between the cement and water and as such the degree of polycondensation of silicon-oxygen anions and compressive strength would improve (Yakovlev et al., 2017). Thus, the higher the concentration of MWCNTs, the greater the compressive strength of the cement would be. However, an excessive amount of MWCNTs may cease the workability of the cement by slowing down the cement hydration rate.

Table 4.9: Compressive strength of the sonicated samples under different curing periods

Sample No.	MWCNTs Content, %	Compressive Strength, MPa (1 Day)	Compressive Strength, MPa (28 Days)
1	0	22.75	34.85
2	0.025	23.76	47.92
3	0.05	28.41	51.88
4	0.075	29.28	45.74
5	0.1	29.61	43.17

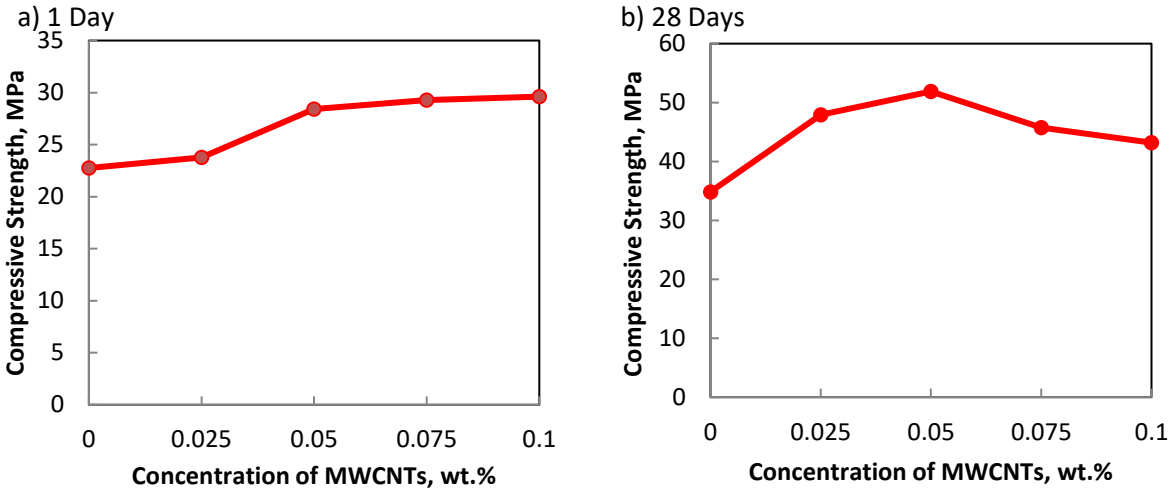


Figure 4.16: Compressive strength of the sonicated samples with: a) 1 Day of curing; b) 28 Days of curing

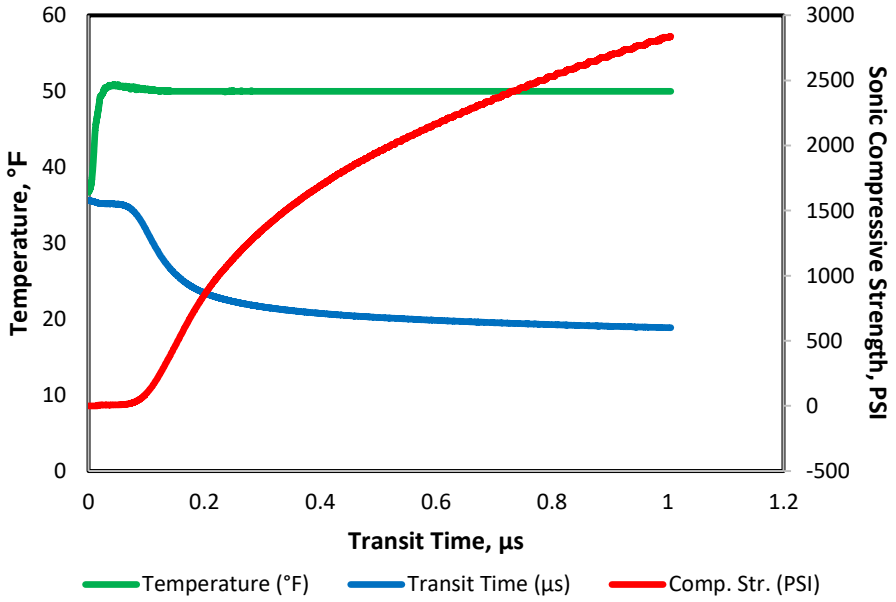
It appeared that within 24 hours (1 day), the cement would rapidly react with water, and the cement strength increases by reducing the cement porosity. However, hydration would continue at a slower rate as time passes and given the fact that the samples with 0.075 wt.% and 0.1 wt.% MWCNTs would hydrate faster in the early stages due to the water adsorption, their compressive strength development would become slower over time.

4.3.6.3. Non-Destructive Compressive Strength

Based on the results obtained from the destructive tests, sonicated sample with 0.05 wt.% MWCNTs gives the highest compressive strength under 1-day and 28-days curing conditions. To determine the development of the cement strength over time

for the sonicated samples, Ultrasonic Cement Analyser Model 3504 was used. To do the test, the apparatus was operated at 16MPa and 50 ºC for 24 hours to simulate the real reservoir condition. Figure 4.17 and 4.18 show the cement strength obtained from the UCA after 24 hours.

0.05 wt.% MWCNTs (S)



0.1 wt.% MWCNTs (S)

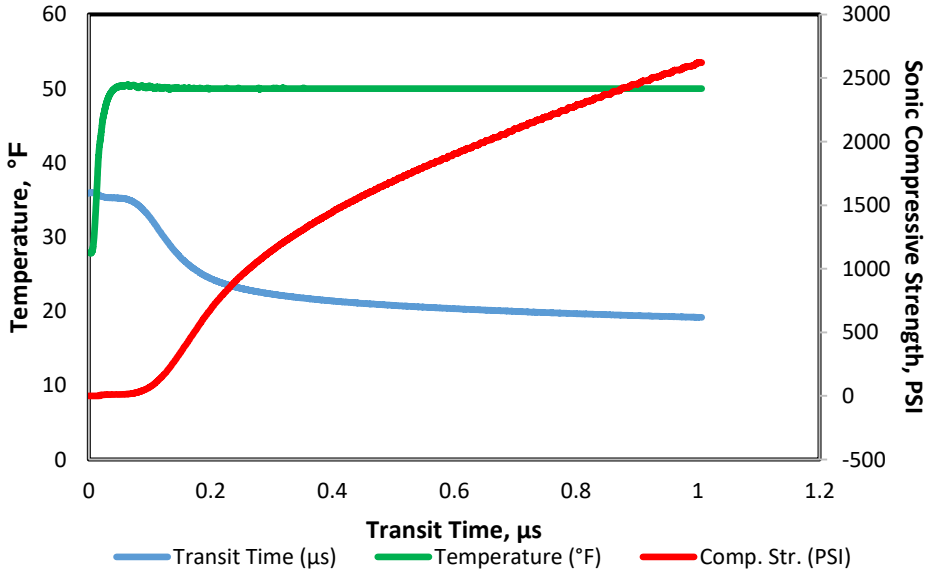


Figure 4.17: Compressive strength of the sonicated cement samples measured using UCA over time

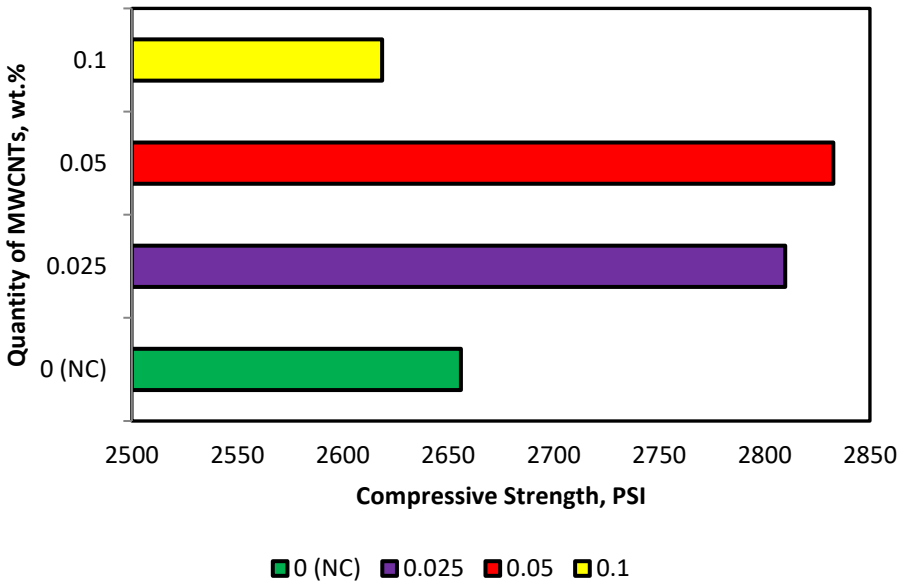


Figure 4.18: Compressive strength of the neat cement and sonicated samples after 24 hours of curing in UCA

The results obtained from the strength measurements using UCA indicated that MWCNTs can improve the compressive strength of the cement except for the case with 0.1 wt.%, which is slightly lesser than NC. It seems that the well-dispersed MWCNTs not only fill up the pore spaces between the cement grains during hydration, but also act as nucleation sites for the calcium silicate hydrate (C-S-H) (Mark and Chan, 2009; Naqi et al., 2019). The decrease in the compressive strength in 0.1 wt% MWCNTs could be due to saturation of the cement with MWCNTs. Above the saturation threshold which appears to be 0.05 wt%, MWCNT does not contribute to the development of the compressive strength anymore.

4.4. Discussion

A good mixing approach is required to ensure that the slurry with MWCNTs gives a consistent result in terms of the rheology and thickening time under different circumstances. Such mixing method would also improve the compressive strength and enhance the pozzolanic activities. In this study, a good dispersion approach based on the sonication was proposed to improve the cement performance using MWCNTs. It was noted without such method, MWCNTs may agglomerate and flocculate easily due to their high surface area and existing strong van der Waals

forces. According to Bharj et al. (2014) who used the sonication approach, proper dispersion of nanomaterials into the cement paste would enhance the compressive strength due to a better interaction between the filler and the matrix.

It also appears that as the amount of MWCNTs increases, the plastic viscosity and the yield stress increase whereas the density of the cement slurry remained the same. This might be linked to the fact that MWCNTs can improve the cement and water interaction, produce more C-S-H, reinforce the cement paste at the nanoscale, and decrease the porosity. Increasing the compressive strength of the cement during the destructive tests, on the other hand, could be due to the proper integration of MWCNTs with the cement particles which increases the toughness and the strength of the cement (Ferro et al., 2011). This was the same conclusion made by Naqi et al., (2019) where they reinforced the cement composites with MWCNTs and indicated that MWCNTs can significantly increase the compressive strength.

In addition, the analysis of the results highlighted that the optimum amount of MWCNTs which can be added to the cement is 0.05 wt.% as it gives a proper rheology and provides the highest strength. This is aligned with the recent study of Mohsen et al., (2017) where it was stated that above a certain quantity, MWCNTs does not take part in the development of the compressive strength due to strong Van Der Vaals forces and induction of particle agglomeration. In fact, without a proper dispersion method, this agglomeration deters hydration of the slurry and as such the strength stops to develop (Saafi et al, 2009; Konsta-Gdoutos et al., 2017). This explains why the manual-mixing samples had a lower compressive strength.

4.5. Conclusion

The effects of MWCNT on the rheological, thermal and strength parameters of the cement were examined in this chapter. Based on the results obtained, the following conclusions were drawn:

- Replacing the cement with 0.25 wt.% MWCNTs was not recommended due to the high plastic viscosity and the yield stress of the slurry.
- As the pressure goes up, the cement hydration would be promoted.
- Given the rheological and the strength behaviours of the cement, the optimum quantity of MWCNTs was determined as 0.05 wt.%.

- Sonication method is a good dispersion method and can lead to a better cement hydration and strength development.
- An excessive amount of MWCNTs negatively affect the microstructures of the cement and reduces the development of the compressive strength.
- Regardless of the MWCNTs quantity, the compressive strength of the cement composite was higher than the neat cement.

Chapter 5: Carbonation of Class G Cement Modified by Nanoparticles

5.1. Introduction

Carbon dioxide (CO_2) is one of the greenhouse gases which leads to trapping of the solar radiations in the atmosphere and thereby resulting in the rise of global warming. Carbon Capture and Storage (CCS) technique, as one of the most promising methods of mitigating the release of CO_2 into the atmosphere, have been successfully tested and implemented around the globe in the past decade. According to the Intergovernmental Panel on Climate Change (IPCC), a well-equipped CCS unit can decrease the emission of CO_2 by 80-90% (IPCC, 2005). CCS is a technology that capture, transport and securely store CO_2 in depleted oil and gas reservoirs, deep saline aquifers or even coal beds. Normally, wells are used as the transport conduit for the storage of CO_2 as part of a CCS project. Thus, wellbore integrity must be vigorous to ensure that CO_2 remains confined and does not seep back to the surface. Cement plays an important role in the wellbore integrity, under these circumstances, which must provide a good resistance against the variation of pressure, temperature and acidity of subsurface layers. Class G cement is widely used in this practice given its significant compatibility with other additives used to give certain functionality to the cement. However, this cement is vulnerable to the acidic environment posed by the presence of CO_2 into the depleted reservoirs. In fact, carbonic acid which is produced because of the reaction between brine and CO_2 in the reservoir can cause cement degradation and seepage of the injected fluid to surface or other subsurface resources (Papadakis et al., 1992; Ridha et al., 2018; Costa et al., 2019).

Numerous studies have been carried out to improve the cement resistance against the attack of CO_2 where modification of the cement with nanoparticles appears to be a promising method as discussed in chapter 2. In this chapter, attempts are made to evaluate the performance of the cement samples modified by NGFs and MWCNTs against the attack of CO_2 in a series of tests known as carbonation. These carbonation

tests were carried out in the presence of wet supercritical CO_2 at the temperature of 50°C and the pressure of 18 MPa. The methodological procedure used and the results obtained are presented and discussed in the following sections.

5.2. Material and Method

5.2.1. Cement Samples

The best cement samples obtained through modification by NGFs and MWCNTs were chosen and used in this stage for the carbonation and post-carbonation tests. The samples prepared by both mixing methods, manual/hand mixing and ultrasonication, were considered to evaluate the effect of the mixing approach on the carbonation rate. All the samples were cured in a water bath under the atmospheric pressure and temperature of 50^{o}C for 24 hours before been tested against the carbonation. Eventually, nine samples were prepared with the ratios reported in Table 5.1.

Table 5.1: Ratio of water, cement, NGFs and MWCNTs used in this study

Sample Type.	Percentage of nanoparticles (wt.%)	Mixing Method	Weight of NGFs (g)	Weight of Cement (g)	Weight of Deionised Water (g)
1	0 (Neat Cement)	-	0	592	260.48
2	0.5 NGFs	H	2.96	589.04	260.48
3	0.5 NGFs	S	2.96	589.04	260.48
4	1 NGFs	H	5.92	586.08	260.48
5	1 NGFs	S	5.92	586.08	260.48
6	0.05 MWCNTs	H	0.30	591.70	260.48
7	0.05 MWCNTs	S	0.30	591.70	260.48
8	0.1 MWCNTs	H	0.59	591.41	260.48
9	0.1 MWCNTs	S	0.59	591.41	260.48

5.2.2. Carbonation Test

Carbonation tests were conducted to examine the performance of nano modified cement against the attack of carbon dioxide (CO_2) under the supercritical state. The cement samples used for the carbonation tests had a size of 2.54 cm x 2.54 cm. A

static reactor was designed and used for the carbonation as shown In Figure 5.1 where the carbonation could be done under the temperature of 50°C and the pressure of 18 MPa. The schematic version of the static reactor is shown in Figure 5.2

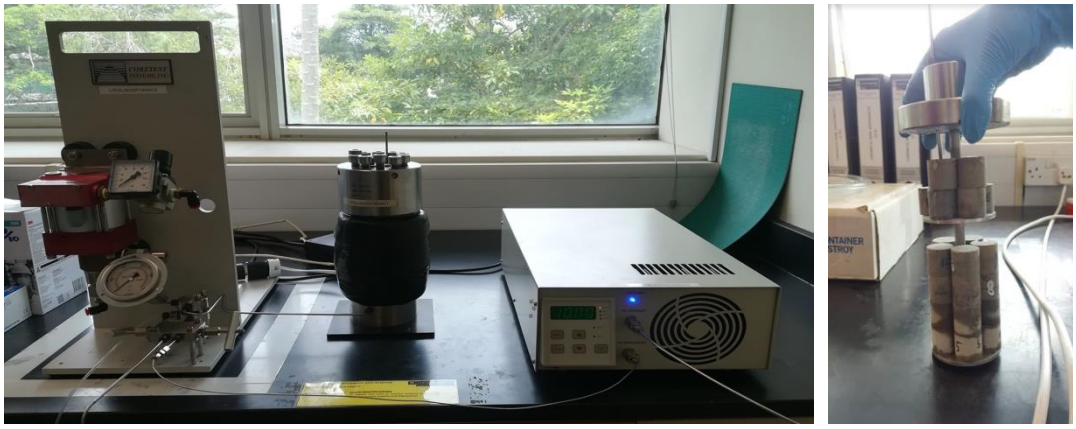


Figure 5.1: The arrangement of cement samples within the inner part of the autoclave

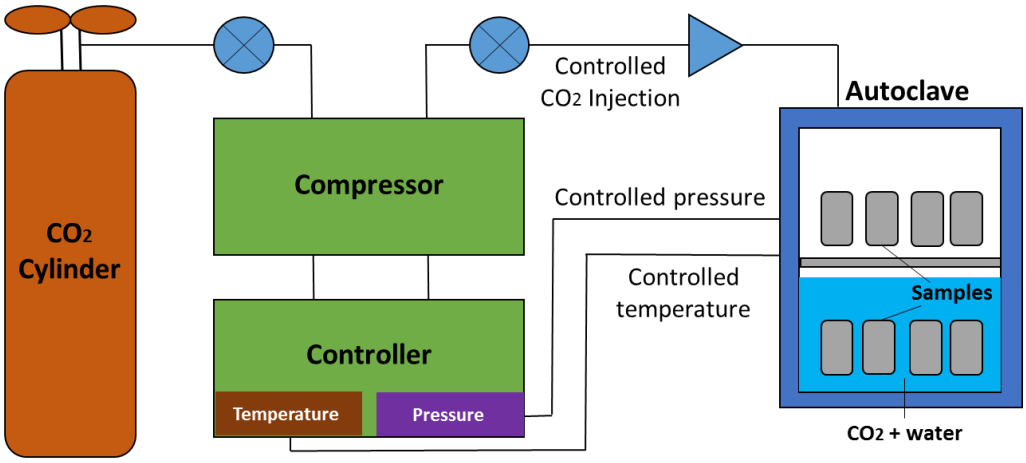


Figure 5.2: Schematic version of the static reactor used in this study for the carbonation test

The reactor consists of a CO_2 cylinder, a supercritical pump (compressor) to inject CO_2, a controller to control the testing conditions, an autoclave to hold the cement samples, metal gas lines and electrical wiring. The autoclave allows the samples to be exposed to water saturated (wet) CO_2 at the bottom and dry supercritical CO_2 at the top.

A total number of 36 samples were prepared and tested as shown in the right side of Figure 5.1 while 9 samples were positioned on the upper portion and 18 samples

were placed on the intermediate and lower portions of the autoclave. Another 9 samples were put outside of the autoclave as non-carbonated samples for the comparison purposes. Fresh water was used instead of brine in the test to accelerate the interactions. According to Barlet-Gouedard et al. (2006, 2007), the concentration of CO_2 dissolved in fresh water was much higher than that of the CO_2 in brine. In fact, the solubility of CO_2 decreases with the increasing salinity. A similar relationship was observed. After sealing the autoclave, supercritical CO_2 was injected using the supercritical pump and hold under the temperature of 50^{o}C and the pressure of ~18MPa for 56 days. The samples were then removed and gone through the post-carbonation stage.

5.2.3. Post-Carbonation Tests

To examine the effect of CO_2 on the nanomodified cements, a series of physical, chemical and mechanical tests were carried out in the post-carbonation stage. These tests were brought into Table 5.2. A flowchart summary is shown in Figure 5.3 to indicate the tests included in the pre- and post-carbonation stages.

Table 5.2: Tests carried out on the cement samples in the post-carbonation stage

Assessment	Test	Equipment	Objective
Physical	Weight Measurement	Analytical Balance	To measure the weight changes
	Porosity Determination	Analytical Balance	To measure the porosity
	Suspension Method	Sension+ PH1 Portable pH Meter	To measure the stability
	Carbonation Depth	Phenolphthalein Indicator	To measure the carbonation depth
Chemical	Microstructural Analysis	Scanning Electron Microscope (SEM)	To investigate the microstructural and mineralogical composition
	Phase Identification	X-ray Powder Diffraction (XRD)	To determine the atomic and molecular structure
	Thermogravimetric Analysis	Mettler Toledo Thermogravimetric Analysis (TGA)	To determine the percentage loss of Portlandite
Mechanical	Uniaxial Compression	Universal Testing Machine (UTM)	To measure the compressive strength

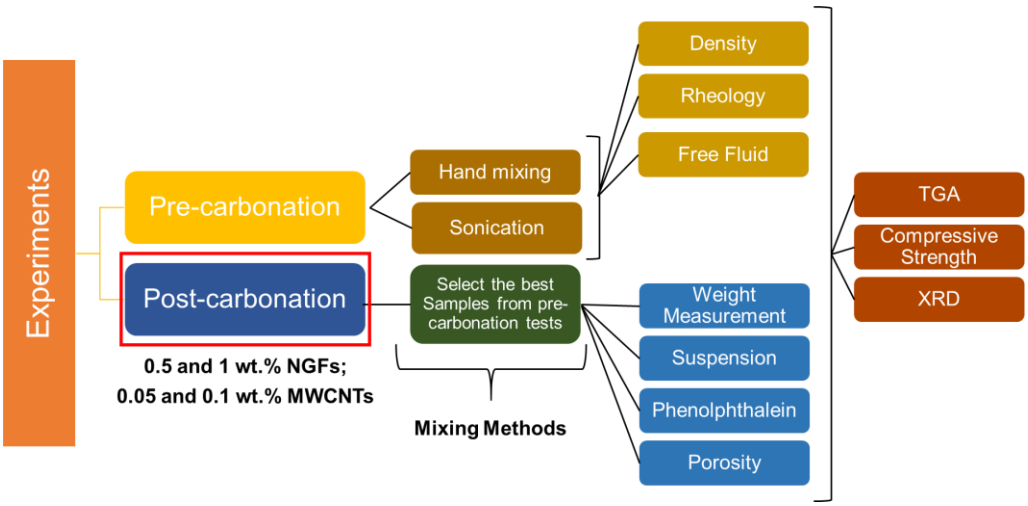


Figure 5.3: A summary of pre- and post-carbonation experiments for this research

5.3. Experimental Results

5.3.1. Weight Measurements

Mass of the samples was measured before and after the carbonation test using the laboratory precision balance, manufactured by Satorius was used. Volume is the fraction of weight divided by density. Hence, any changes in the cement weight would affect the cement volume. The possible factors that would change the volume are nonreactive cement fractions, hydration products formed, capillary water, gas bubbles and slurry shrinkage (Brouwers, 2011). It was observed that the empty volumetric fraction of the cement matrix changes over time, mainly due to the consumption of non-hydrated cement, reaction with the capillary water and production of the new products.

Hence, in this case, since all the samples were kept in a supercritical CO_2 confined space, the mass increase would be related to the addition of an external reagent to the system (carbon dioxide and its derivatives) forming calcium carbonate in the matrix. This is due to the carbonation reactions, where calcium carbonate is formed through the reactions of CO_2 with the Portland cement hydrated products. Figure 5.4 shows the cement samples and the analytical balance scale used in this study.

Figure 5.4: a) carbonated cement samples; b) Analytical balance used to measure the cement weight

5.3.1.1. Before and After Carbonation

The results obtained from measuring the weight of the samples after 28 days of exposure to wet CO_2 indicated that there is an increase in the weight of the samples as reported by Table 5.3 and shown in Figure 5.5.

As it seen in Table 5.3, After 28 days of exposure, the weight of all samples increases while the highest value belongs to the sample with 0.05 wt.% MWCNTs followed by 1 wt.% NGFs. It appears that the weight/mass increase is posed by the carbonation reactions where calcium carbonate ($CaCO_3$) is formed through CO_2 reactions with Portland cement (Yang et al., 2016; Sena Costa et al., 2017).

Table 5.3: Variation of the samples weight after 28 days of carbonation

Sample	Weight (g)		
	Before	After	Difference, %
Neat Cement	21.42	27.08	+ 26.42
0.05 wt.% MWCNTs	22.15	28.24	+ 27.49
0.1 wt.% MWCNTs	22.41	27.62	+ 23.24
0.5 wt.% NGFs	21.93	27.31	+ 24.53
1 wt.% NGFs	21.94	27.82	+ 26.80

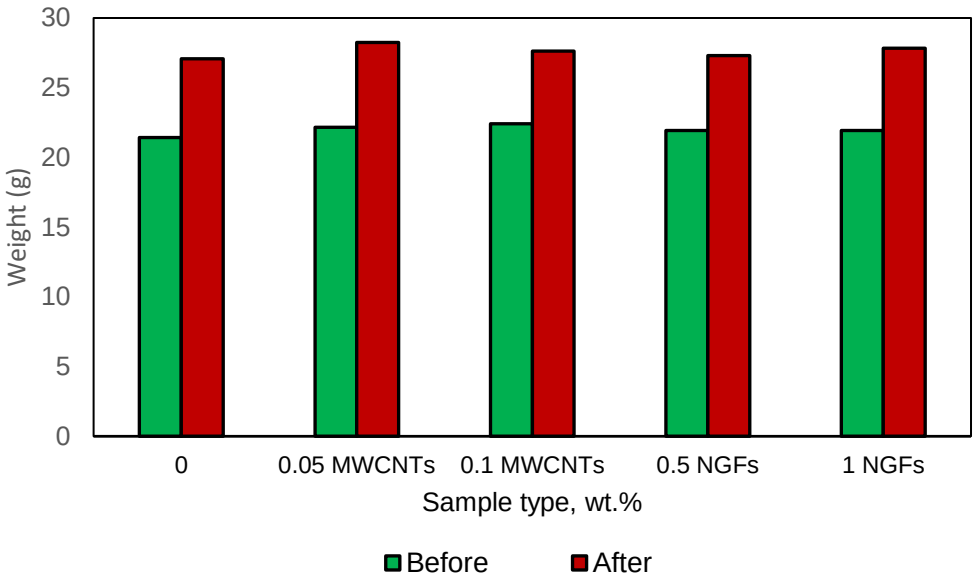


Figure 5.5: Weight of the samples before and after 28 days of carbonation

5.3.1.2. Carbonation Period

To evaluate the effect of the carbonation period on the performance of the samples, the same set of the samples were gone through the carbonation for 56 days. The results obtained are given in Table 5.4 and shown in Figure 5.6.

Table 5.4: Comparison of the results obtained after 28 days and 56 days of carbonation

Sample, wt.%	28 days, g			56 days, g		
	Before	After	Difference, %	Before	After	Difference, %
0	23.40	27.45	+ 17.31	21.42	27.08	+ 20.90
0.05 MWCNTs	22.15	28.24	+ 21.56	22.48	27.33	+ 21.57
0.1 MWCNTs	22.41	27.62	+ 18.86	22.26	27.51	+ 23.58
0.5 NGFs	21.93	27.31	+ 19.70	23.19	28.03	+ 20.87
1 NGFs	21.94	27.82	+ 21.14	22.88	27.75	+ 21.28

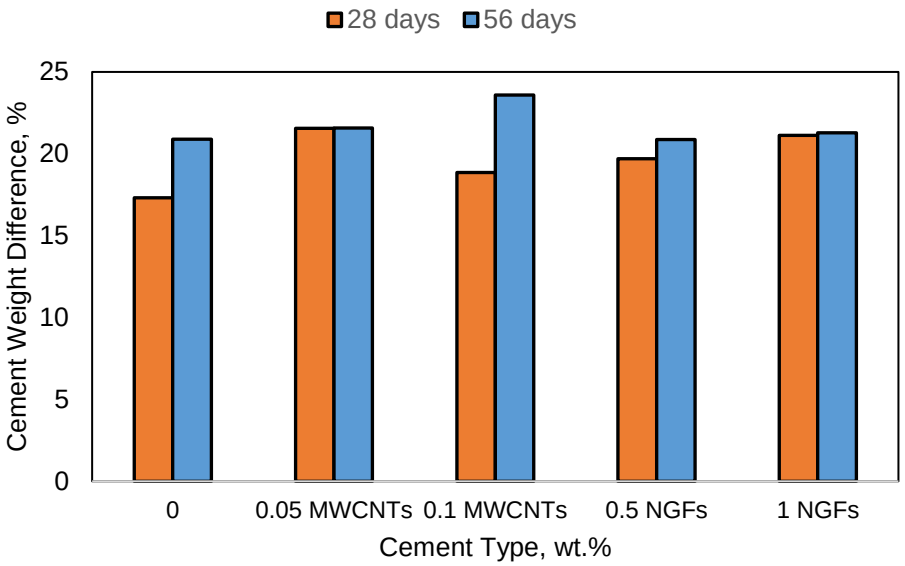


Figure 5.6: Weight of the samples before and after 28 and 56-days of carbonation

The results obtained indicated that the weight/mass of the samples increases even after 56 days of carbonation. The highest increase, however, belongs to the samples with 0.1 wt.% of MWCNTs, followed by 0.05 wt.% MWCNTs. It appears that the weight increment rate goes higher with the carbonation period. Nevertheless, it seems that all the samples are still in the carbonation stage and bicarbonation was not started yet. To evaluate the impact of the carbonation on the cement, the results were compared to those samples that were not carbonated.

5.3.1.3. Carbonated vs Non-Carbonated Samples

Two different sets of samples were prepared and left aside for 28 days and 56 days for comparison with those that were exposed to CO_2. This could help us to determine the amount of changes induced in the weight by the carbonation within different time scales. The results of this comparison are given in Table 5.5 and shown in Figure 5.7.

Table 5.5: Comparison of the variation in the cement weight without carbonation

Non-Carbonation	28 days, g			56 days, g		
Sample type	Before	After	Difference, %	Before	After	Difference, %
0	21.34	21.22	- 0.56	23.47	22.51	- 4.09
0.05 MWCNTs	22.01	21.87	- 0.64	22.33	22.27	- 0.26
0.1 MWCNTs	22.43	22.13	- 1.34	22.40	22.39	- 0.04
0.5 NGFs	22.08	22.00	- 0.36	23.20	22.45	- 3.23
1 NGFs	21.75	21.68	- 0.32	22.34	21.92	- 1.88

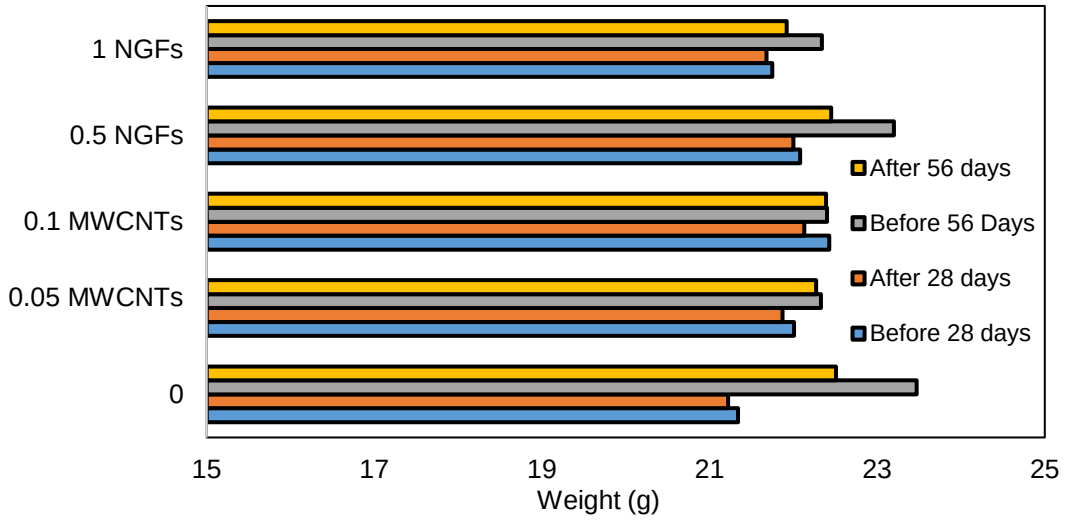


Figure 5.7: Comparison of the variation in the cement weight without carbonation

Looking at Table 5.5, it seems that all the samples had a minor weight reduction and the highest difference between belongs to the neat cement after 56 days. This weight loss could be related to the environmental deterioration of the cement. The cement tends to undergo chemical alteration due to the interaction with the surrounding environment which reduces the strength of the cement binder. By adding nanoparticles, the cement matrix seems to have a better resistance against the cement deterioration posed by the atmospheric condition. Compared to the non-carbonated samples, the weight of the carbonated samples increased considerably, as shown in Figure 5.8. After 56 days, the non-carbonated samples, which were cured

under the room temperature, showed only minor differences in the weight. In fact, the weight increase observed in the carbonated samples could be due to the formation of $CaCO_3$ and the carbonation process that took place in the cement. It should be noted that if bicarbonation starts, $CaCO_3$ will leach-out of the samples and the density would significantly decrease.

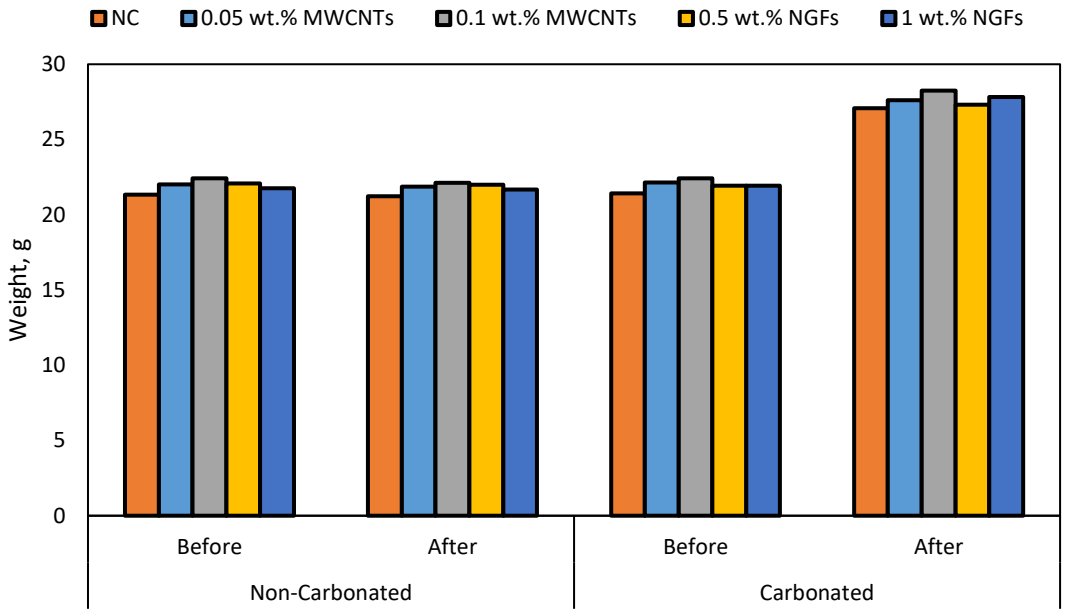


Figure 5.8: Weight comparison of MWCNTs and NGFs nano-modified cements before and after 56 days of carbonation

In general, the precipitation of $CaCO_3$ in the cement system through the chemical reactions causes an increase in the mass of the samples (Costa et al., 2018). It appeared that all the samples were carbonated with the same rate and as such it was not easy to indicate which sample(s) performed better during the carbonation based on the weight analysis. To support the arguments, suspension tests were carried out to check the pH and the carbonation depth of the carbonated samples.

5.3.2. Suspension Test

Measuring pH is one of the effective methods to determine the occurrence of carbonation in the cement samples. After the carbonation period, the pH of the water inside the autoclave was measured using a Sension+ PH1 Portable pH Meter,

as shown in Figure 5.9a. The pH before and after the carbonation was 6.9 and ~7.2 respectively. This was due to the chemical reactions between the alkaline cement and acidic CO_2 which creates a neural environment. This result was then confirmed with the pH indicator strips shown in Figure 5.9b.

a) b)

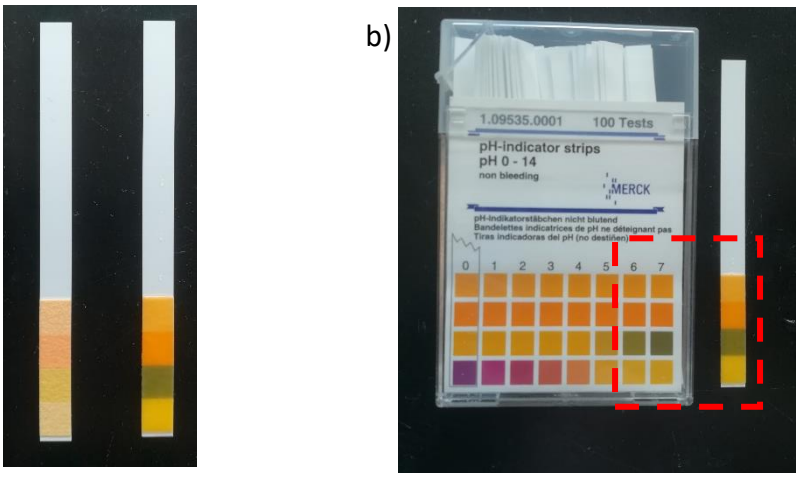


Figure 5.9: a) Original strip and b) the tested strip with the colour indicating the pH of 7

After the pH measurement of water, the cement pH was measured using the suspension method as per the approach proposed by Rasanen and Penttala, (2004). The measurement was done by mixing the powdered cement samples with a solvent and conducting the pH test on the suspension. This method has been widely used to measure the pH of concrete (Manso and Aguado, 2017; Pu et al., 2012). To do the test, 3 g of the samples with 56 days of carbonation was mixed with 10ml of distilled water. The pH of the solution was then examined using the pH meter. Figure 5.10b shows the results obtained from the suspension tests on the non-carbonated and carbonated samples.

It is observed that the non-carbonated samples have a higher pH (an alkaline environment) compared to the carbonated cements. It should be recalled that in a pore solution, alkaline calcium hydroxide ($Ca(OH)_2$) is the major hydroxyl ion supplier. The amount of $Ca(OH)_2$ in the cement determines the durability of the cement against the carbonation since it is attacked by CO_2 first. Thus, when the pH of the cement drops (become more acidic), $Ca(OH)_2$ is consumed by the carbonation process and calcium carbonate is formed, which increases the mass of the cement

(Ghahari et al., 2016). Having said that, it seems that the sample with 0.1 MWCNTs has the highest pH difference, with the highest carbonation.

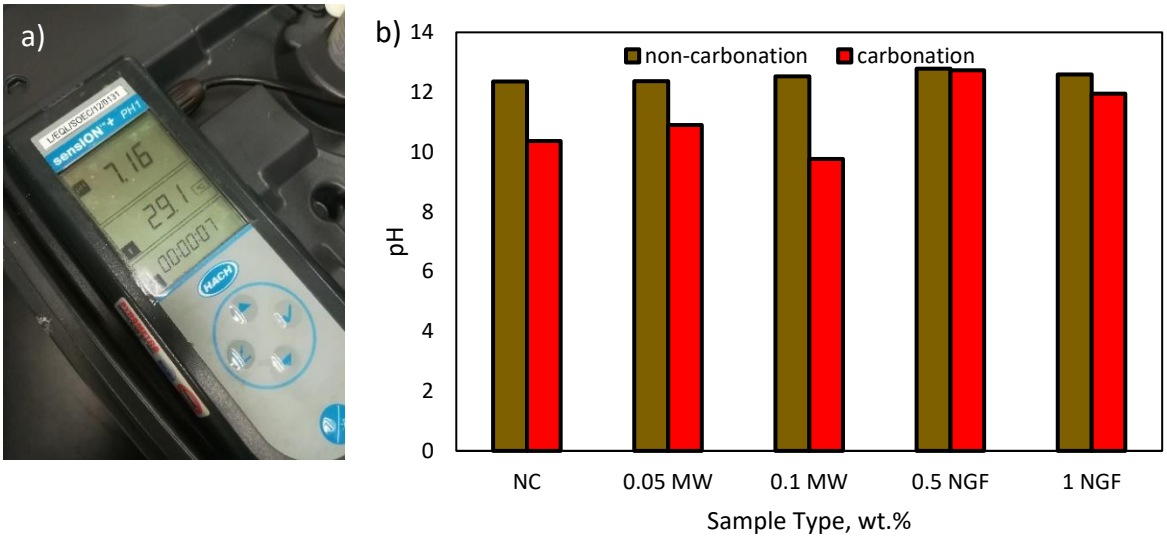


Figure 5.10: a) pH Meter; b) Comparison between the non-carbonated and carbonated samples

5.3.3. Phenolphthalein Test

After the carbonation test, all the samples were removed from the autoclave and their weights were checked. This was followed by cutting them in half in the longitudinal direction, cleaning their surface and applying the Phenolphthalein solution on their surface. To prepare the Phenolphthalein solution, 70ml of ethanol was diluted in 30ml deionized water before adding 1.5g of phenolphthalein powder. Colour of this solution/solid turns into purple/magenta once the pH goes above 10.5. It remains colourless when the pH is less than 10.5. In fact, it would turn into purple in the presence of alkaline (non-carbonated) regions while its colour does not change in the carbonated region. To properly analyse the carbonated regions highlighted by the Phenolphthalein solution, an image analyser called Image J was used. This software is able to quantify the carbonated area by converting the image into 8-bit format and highlight the affected area (see Figure 5.11). Figure 5.12 shows the carbonated part of the neat cement sample in different scales.

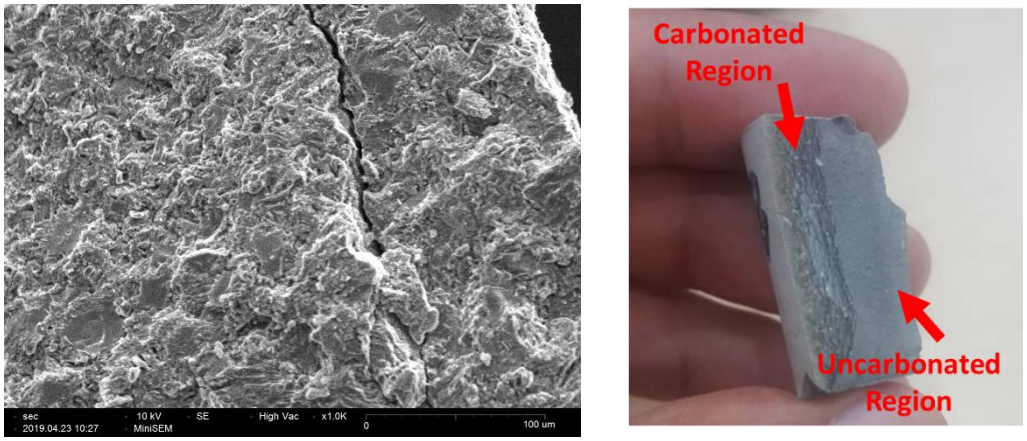


Figure 5.11: Carbonated neat cement sample after carbonation in different scales

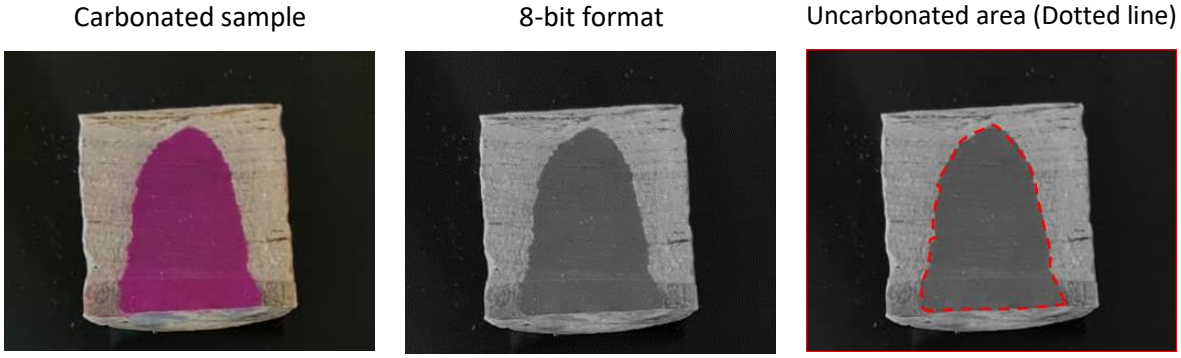


Figure 5.12: Phenolphthalein test and carbonated areas highlighted by the image analyser

5.3.3.1. Carbonation Depth

Those samples exposed to wet $scCO_2$ for 56 days were tested in this stage using the Phenolphthalein solution to evaluate the effect of the carbonation depth. This category was chosen as it was exposed to the acidic environment for a longer period of time. The results obtained are given in Table 5.6 and shown in Figure 5.13.

The results obtained indicated that the sample with 0.05 wt.% MWCNTs and 0.5 wt.% NGFs would give the best performance against the attack of CO_2. These samples were the ones with the best performances even under the pre-carbonation stage where the changes of the compressive strength and the amount of portlandite left in the samples were reported. It appears that the presence of nano scale particle will accelerate the pozzolanic reactions and create a dense/consolidated cement matrix which can resist against the attack of $scCO_2$.

Table 5.6: Carbonated/Uncarbonated areas in the samples after 56 days

Cement Type	Total Surface Area (cm^2)	Unaffected Area (cm^2)	Carbonated Area (cm^2)	Carbonated Area (%)
Neat cement (NC)	6.45	3.426	3.02	46.88
0.05 MWCNTs (S)	6.45	3.977	2.473	38.34
0.1 MWCNTs (S)	6.45	3.311	3.139	48.67
0.5 NGFs (S)	6.45	3.718	2.732	42.36
1 NGFs (S)	6.45	3.342	3.108	48.19

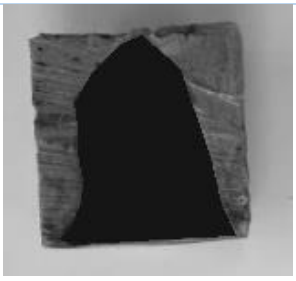
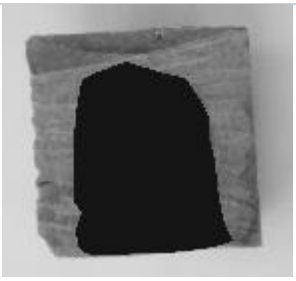
Cement Type	Neat Cement	MWCNTs (0.05 wt%)	MWCNTs (0.1 wt.%)
Carbonated Image			
Cement Type	Neat Cement	NGFs (0.5 wt%)	NGFs (1 wt.%)
Carbonated Image			

Figure 5.13: Cement samples after 56 days of exposure to CO_2

It was also found that as the quantity of nanoparticles increases, the depth of the carbonation increases. This could be due to the nanoparticle's agglomeration in high percentage. Presence of aggregates can lead to the creation of capillary pores which increase the risk of carbon ions infiltration into the samples. This is the very same results obtained after 28 and 56 days of the carbonation as reported in Table 5.7,

although it appears that environmental setup posed for 28 days was harsher than 56 days.

Table 5.7: Carbonation depth (C) of the samples after 28 and 56 days

Cement Type	C in percentage, %	
	28 days	56 days
Neat cement (NC)	55.19	46.88
0.05 MWCNTs (S)	56.00	38.34
0.1 MWCNTs (S)	65.90	48.67
0.5 NGFs (S)	56.47	42.36
1 NGFs (S)	64.30	48.19

5.3.3.2. Mixing Method

The performance of the mixing methods, the hand mixing (H) and sonication (S) were also analysed to see if a proper dispersion method is required to uniformly distribute the nanoparticles into the cement matrix. The results obtained are given in Table 5.8 and shown in Figure 5.14.

The result obtained indicated that the samples prepared by the hand mixing method have an overall greater carbonation depth compared to the sonicated samples. The greatest carbonated area belongs to the samples with 1 wt.% NGFs (H), followed by 0.1 wt.% MWCNTs (H). On the other hand, the carbonated area observed in the samples with 0.05 wt.% MWCNTs (S) and 0.5 wt.% NGFs (S) was minimum. This indicates that a good dispersion is crucial to improve the cement performance when it comes to nanomodification. In fact, when the nanoparticles are distributed more evenly, the cement matrix structure is enhanced and the cement strength increases. Due to the inconsistency created by the hand mixing, all the samples might have irregular and larger cement pores which favour the infusion of CO_2 into the cement matrix, causing severe degradation. As a result, a greater carbonation depth was observed in the hand mixing samples.

Table 5.8: Comparison of the carbonation depth in the samples with different mixing methods

Cement Type	Carbonated area (%)	
	Sonication (S)	Manual-Mixing (H)
0.1 MWCNTs	48.67	52.42
0.05 MWCNTs	38.34	47.21
1 NGFs	48.19	59.71
0.5 NGFs	42.36	50.42
Neat cement	46.88	

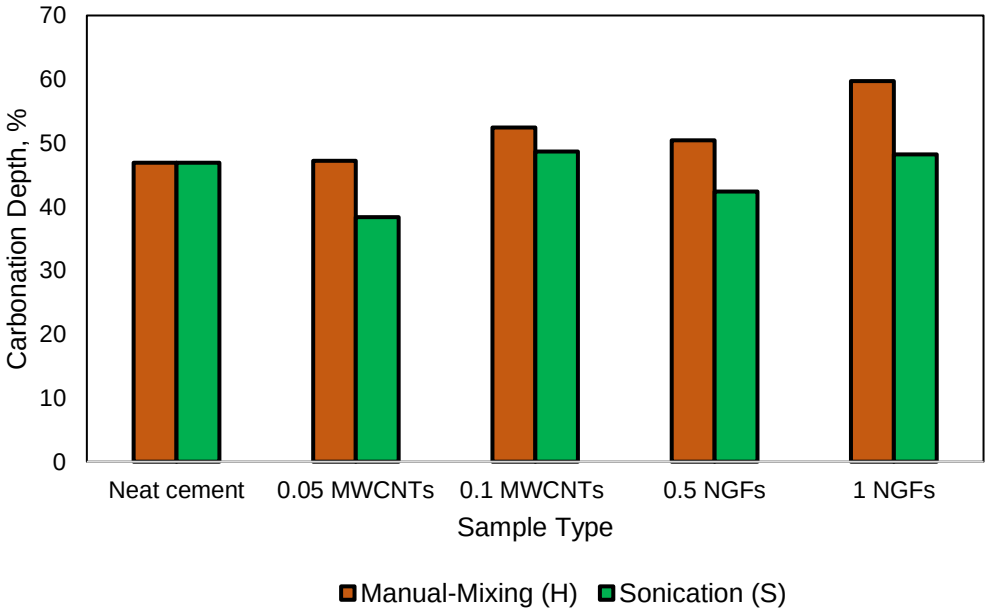


Figure 5.14: Carbonation depth for different cement types

5.3.4. Porosity Determination

To measure the cement porosity before and after the carbonation, the Archimedes principle was used by assuming that the volume of evaporable water in a wet sample is equal to the volume of the voids within the sample (Unosson et al., 2014).

Before determination of the total porosity, the cement samples were dried in the oven, at 100°C for 24 hours. They were then immersed in water for 24 hours before measuring their weight. This was followed by estimation of the porosity from the ratio between the weights of the samples before and after the carbonation (Zhao et

al., 2014), using Eq.(5.1). The results obtained from these measurements are summarised in Table 5.9 and Figure 5.15.

$$P = \frac{(W_b - W_d)}{W_b} \times 100 \quad (5.1)$$

Table 5.9: Measurement of the cement porosity after carbonation

Cement Sample	Dry, g	Wet, g	Porosity, %
Neat cement	11.7	12.94	10.6
0.05 MWCNTs (H)	11.5	12.77	11.0
0.05 MWCNTs (S)	11.65	12.91	10.8
0.1 MWCNTs (H)	13.55	14.91	10.0
0.1 MWCNTs (S)	14.26	15.62	9.5
0.5 NGFs (H)	11.75	12.98	10.5
0.5 NGFs (S)	12.32	13.58	10.2
1 NGFs (H)	12.34	13.7	11.0
1 NGFs (S)	10.7	11.81	10.4

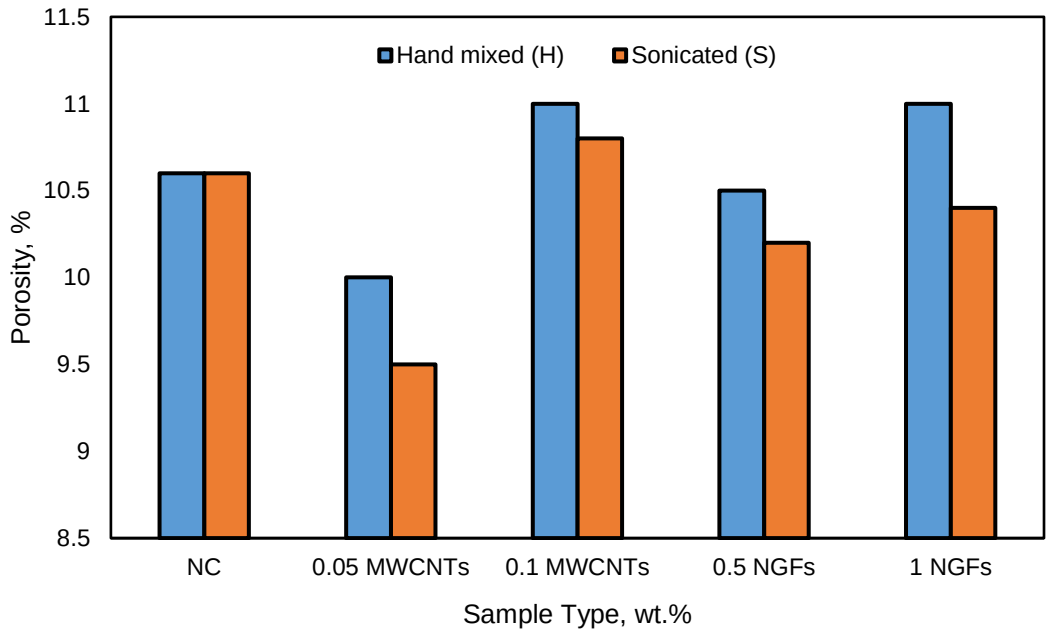


Figure 5.15: Comparison of the sample porosity for sonicated and hand-mixed samples after carbonation

Looking at Figure 5.15, it appears that the samples with 0.1 wt.% MWCNTs and 1 wt.% NGFs had their porosity increased. This could be due to the severe carbonation that these two samples were gone through. It should be noted that 1 wt.% of the cement was replaced by NGFs which may result in poor hydration and development of the cement strength. As a consequence, the cement particles were not fully integrated to reduce the porosity. Technically speaking, cement with nanoparticles would have a lower porosity than the neat cement. This is mainly because the nanoparticles can reduce the cement porosity by filling up the pores during the hydration (Shah et al., 2018). Thus, the percentage of nanoparticles added to the cement is crucial as it may enhance or reduce the cement porosity and strength.

It was also observed that a good dispersion method can enhance the cement performance by improving the cement strength and reducing the porosity. In fact, it was observed that the sonicated (S) samples are much durable compared to the manual-mixed (H) samples as given in Table 5.9.

5.3.5. X-Ray Diffraction (XRD)

X-ray diffraction test were performed on the samples using Rigaku Miniflex X-Ray Diffractometer (XRD). It is a type of desktop XRD which is capable of measuring powder diffraction patterns from 3 to 145° in 2 theta scanning range. The scanning was run within the range of 50° - 80° for every 0.2 s in the port rotation of 15rpm. The software used for the phase identification was Match! of Crystal Impact. XRD tests was done to examine the level of the carbonation in the samples. The results obtained are given in Table 5.10 and shown in Figure 5.16.

Portlandite $Ca(OH)_2$ is the main crystalline phase that can be used for the characterization of the carbonated samples given its severe reaction with CO_2. In fact, after carbonation, it is expected to see a decrease in the amount of portlandite and C-S-H because they may react with CO_2 and produce calcite and aragonite (Galan et al. 2015; Martinez-Ramirez et al. 2003).

Table 5.10: Comparison of $CaCO_3$ minerals in the carbonated samples

Sample Types, wt.%	Calcite, %	Aragonite, %
Neat Cement (NC)	20.3	-
0.05 MWCNTs (H)	45.4	54.6
0.05 MWCNTs (S)	44.3	55.7
0.1 MWCNTs (H)	34.5	47.4
0.1 MWCNTs (S)	45.4	52.6
0.5 NGFs (H)	38.5	50.2
0.5 NGFs (S)	33.6	50.5
1 NGFs (H)	36.6	54.6
1 NGFs (S)	34.2	54.2

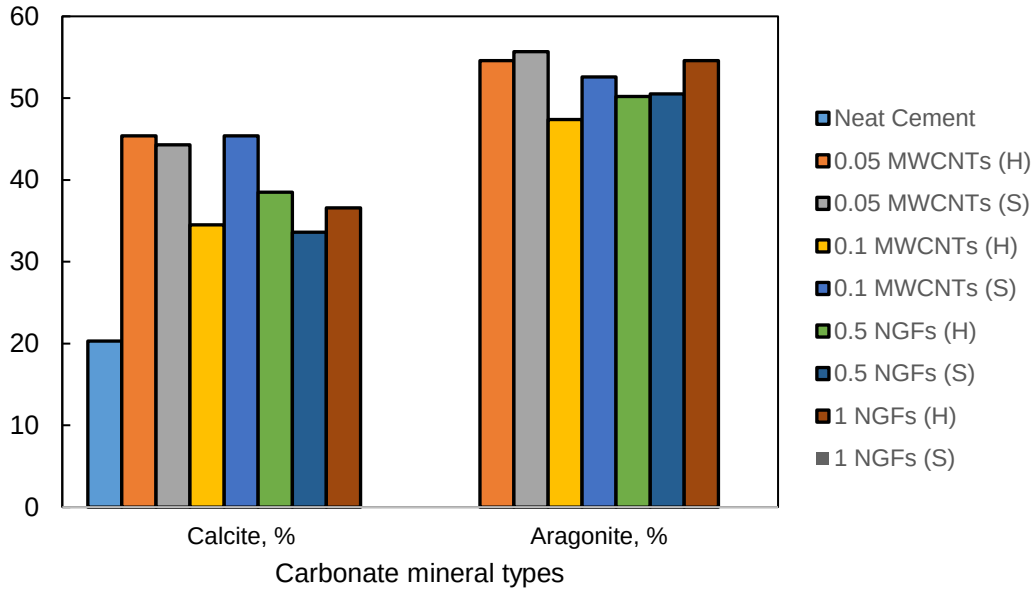


Figure 5.16: Carbonated minerals distribution in different cement samples

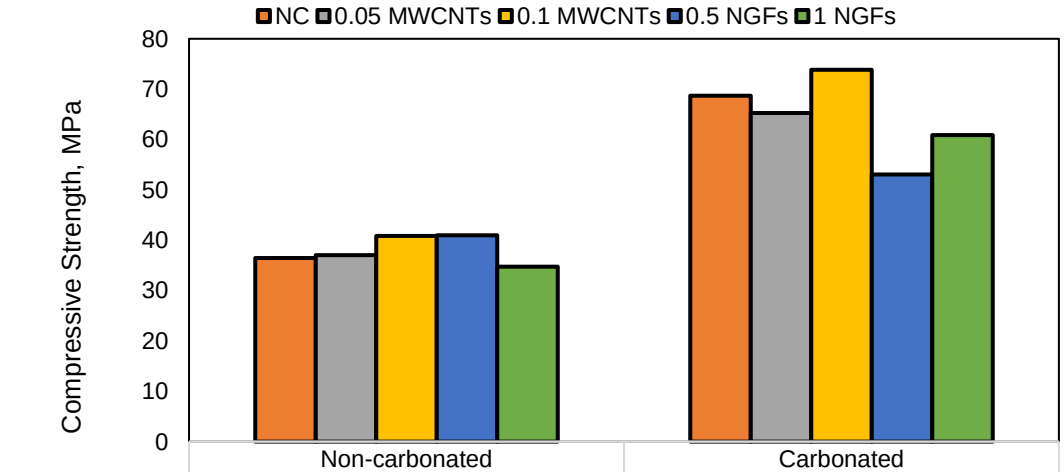
Looking at Table 5.10 and Figure 5.16, calcite was observed in every carbonated samples. This is due to the consumption of $Ca(OH)_2$ which produces $CaCO_3$ while calcite is the most abundant crystalline phase of $CaCO_3$. Calcite, generally, has a crystalline arrangement that requires lesser energy for the crystallization compared to aragonite. Thus, in the region where the aragonite is formed, the carbonation process is much aggressive (Galan et al. 2015). Having said that, it appears that the samples with 0.5 wt.% NGFs has the lowest amount of aragonite. The results shown

are align with the outcome of the porosity test where the sample with 0.5 wt.% NGFs had the lowest porosity.

5.3.6. Compressive Strength

The compressive strength of the samples was also measured before and after the carbonation. It should be noted that due to the consumption of the portlandite, calcium carbonate ($CaCO_3$) is produced that will fill up the pores and improves the strength. As time passes and portlandite is completely consumed, the bicarbonation starts and the cement would lose its integrity. In fact, the strength development in the carbonation stage is the sign of the carbonation rate. Thus, the faster the carbonation rate is and the lower the resistance of the cement is against the CO_2 attack, the higher the compressive strength would be.

To examine the strength development after the carbonation, the sonicated samples exposed to CO_2 for 56 days were chosen. The results obtained are shown in Figure 5.17.



	Non-carbonated	Carbonated
NC	36.43	68.71
0.05 MWCNTs	37.03	65.25
0.1 MWCNTs	40.86	73.86
0.5 NGFs	40.99	53.07
1 NGFs	34.75	60.89

Figure 5.17: Compressive strength of the samples before and after carbonation

Looking at Figure 5.17, it seems that the compressive strength was developed in all the samples after exposure to CO_2, indicating that the carbonation took place. Before

carbonation, the samples with 0.5 wt.% NGFs and 0.1 wt.% MWCNTs had the highest strength. However, after 56 days of carbonation, the samples with 0.5 wt.% NGFs and 0.05 wt.% MWCNTs had the lowest strength development. As it was mentioned earlier, the higher the resistance of the samples is against the carbonation, the lower the strength would be due to the lesser production of $CaCO_3$. It was also concluded that the sample with 0.5 wt.% NGFs is the best sample before and after the carbonation. Having said that it appears that NGF is a better option than MWCNT to reinforce the cement for CO_2 storage sites. Given the fact that NGFs are significantly cheaper than MWCNTs, they would be a great option to ensure that CO_2 is remained confined once injected in the storage sites.

5.3.7 Thermogravimetric Analysis (TGA)

TGA is an analytical technique used to determine the thermal stability of materials or their components by monitoring the weight change that takes place as the sample is heated at a constant rate. The set up used to run the TGA on the carbonated samples was the same set up used earlier in the previous chapters to evaluate the amount of portlandite left in the uncarbonated samples. However, for the carbonation study, the temperature was varied from 20 to 1000°C. Initially, the amount of Portlandite left in the sample was determined. The weight loss in the samples was then recorded after the dehydroxylation of portlandite to determine the amount of portlandite left after the carbonation. According to Thiery et al (2007) and Kocaba et al. (2009), the slope of the curves changes somewhere between 520 to 780°C which corresponds to the release of CO_2 by decomposition of $CaCO_3$ while Huijgen et al. (2005) and Huntzinger (2006) suggested the temperature range of 550-800◦C to accurately detect the phenomenon. Hence, for the purpose of this study, the reading was recorded from 520 to 800◦C. The equation used to determine the amount of Portlandite was similar to the one used in the previous chapters (Eq 3.3). The results obtained were presented is shown in Figure 5.18, where the weight loss and the amount of portlandite for different temperature range are depicted.

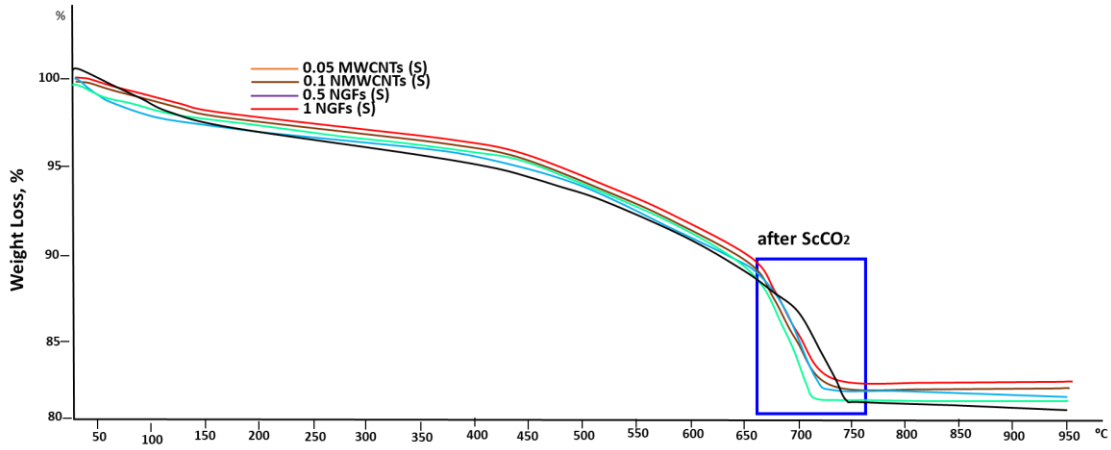


Figure 5.18: TGA plots of MWCNTs and NGFs based cements with different mixing methods

5.3.7.1. Different Thermal Phases

Two thermal phrases (400-500°C for dehydroxylation of portlandite and 550-800°C for calcium carbonate ($CaCO_3$) decomposition) were considered as part of the TGA analysis with the results given in Table 5.11 and shown in Figure 5.19.

Table 5.11: Weight loss of different cement samples in different thermal phases

Cement Types, wt.%	Weight loss, %	
	400-500°C	550-800°C
Neat cement (NC)	1.20	6.95
0.05 MWCNTs (S)	1.40	11.73
0.1 MWCNTs (S)	1.76	11.55
0.5 NGFs (S)	1.16	8.26
1 NGFs (S)	1.35	11.35

As it is seen in Table 5.11, the lowest weight loss is observed in the neat cement for both phases. It was also revealed that the sample with 0.5 wt% NGFs has the lowest amount of portlandite in its structure while the cement with 0.1 wt.% MWCNTs has the highest amount. This result is aligned with the finding of the compressive strength as discussed earlier in section 5.3.6.

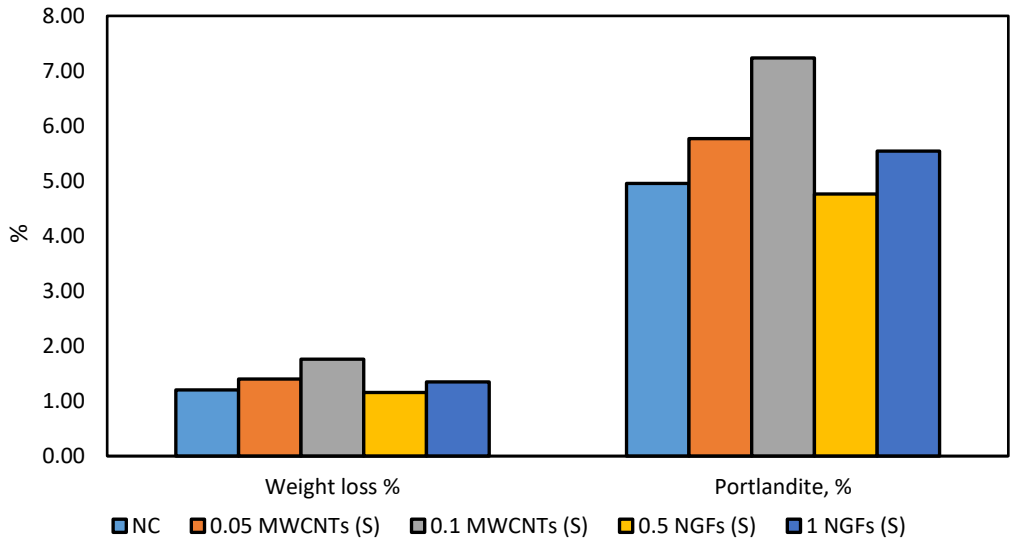


Figure 5.19: Weight loss and the amount of portlandite left in the samples in the dehydroxylation phase (400-500°C)

As it was mentioned earlier, the mass loss in the second thermal phase indicates the amount of CO_2 released by the decomposition of $CaCO_3$ (Um and Ji-Whan, 2017). In other words, a high mass loss would indicate that $scCO_2$ interacts significantly with the cement, resulting in a huge level of carbonation. It was then observed that the samples with MWCNTs had a higher weight loss in the second thermal phase.

5.3.7.2. Comparison of Uncarbonated and Carbonated Samples

To evaluate the amount of carbonations in the samples, the results obtained from the TGA of uncarbonated and carbonated samples were compared. The results obtained are given in Table 5.12 and shown in Figure 5.20.

Table 5.12: Comparison of Portlandite quantity in uncarbonated and carbonated samples

Cement Type	Amount of Portlandite, %		
	Uncarbonated Samples	Carbonated Samples	Difference, %
Neat Cement (NC)	12.58	4.95	7.63
0.05 MWCNTs (S)	15.76	5.77	9.99
0.1 MWCNTs (S)	13.32	7.23	6.09
0.5 NGFs (S)	13.35	5.61	7.74
1.0 NGFs (S)	16.79	6.35	10.44

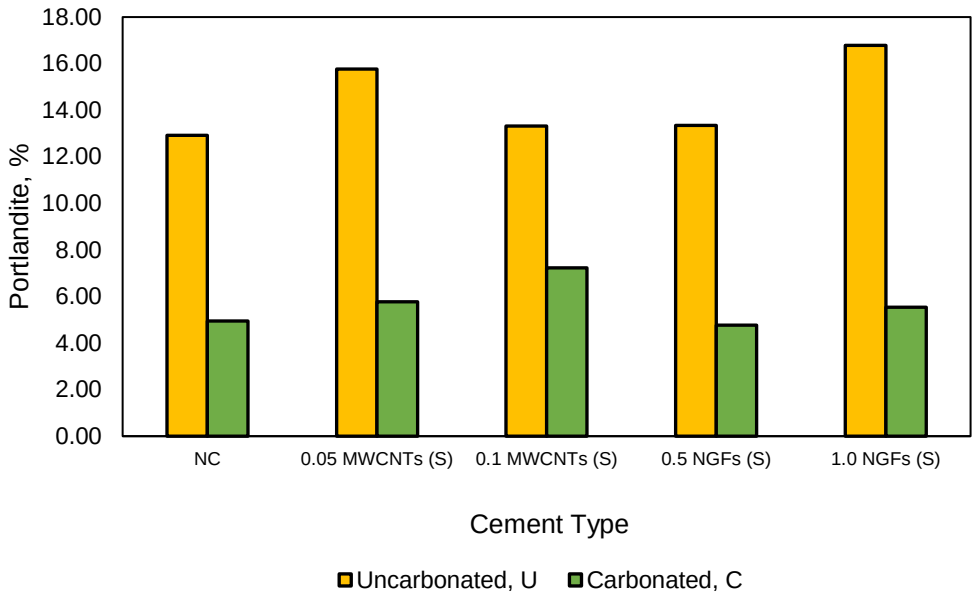


Figure 5.20: Comparison of Portlandite quantity in uncarbonated and carbonated samples

As seen in Figure 5.20, the sample with 1.0 wt.% NGFs produces the most Portlandite before carbonation and the same sample has a huge amount of portlandite consumptions in the carbonation stage. In fact, the highest degree of carbonation was observed in the samples with 1.0 wt.% NGFs as the difference between the amount of portlandite left in the sample before and after the carbonation was around 10%.

5.4. Discussion

Carbon dioxide (CO_2), in the presence of water, forms a corrosive medium that reacts with the cement hydrated products in a process known as the carbonation. This process enhances the weight of the cement, mainly because of the formation of calcium carbonate ($CaCO_3$). However, further diffusion of CO_2 into the cement and its reaction with the calcium ions will reduce the integrity of the cement and result in total disintegration. This phenomenon causes changes in the pH of the cement which can be detected by the phenolphthalein tests.

The results obtained from the measurements made on the carbonated samples indicated that none of them reached the bicarbonation stage while the carbonation process improved their microstructure, density and compressive strength. This was

the same conclusion made by Lim and Mondal (2015) where they did an accelerated carbonation test on Portland cement modified by nano-silica for 21 21 days. They indicated that adding 9.3 wt% nanosilica can reduce the total carbonation of the cement pastes.

Different degree of carbonation, however, was observed in different samples modified by nanomaterials. It appears that adding 0.5 wt.% NGFs or 0.05 wt.% MWCNTs is the best approach to improve the cement resistance. Yeon et al. (2019) did a same series of studies on the cement treated by nanosilica and exposed to CO_2 for 62 days. They concluded that adding 2 wt% nano-silica can improve the cement performance against the attack of CO_2. It was concluded that NGFs and MWCNTs may provide the same performance with a lower dosage.

Technically concluding, MWCNTs showed a better performance compare to NGFs, given their ability to control the morphology of the calcium carbonate crystal of the carbonation products in the hydrated cement paste, which could create fiber-like reinforcements in the cement paste (Yan et al., 2016). Given the fact that NGF is significantly cheaper than MWCNTs, one may also consider NGFs for the cement reinforcement in CO_2 storage sites.

5.5. Conclusion

In this study, two mixing methods were tested and the carbonation test was carried out to evaluate the performance of MWCNTs and NGFs on the reinforcements of the class G cement. It was then concluded that:

- A good dispersion method can help to improve the cement properties once nanomaterials are considered.
- Under a similar pressure and temperature condition, relative humidity of the environment controls the carbonation rate, which can affect the overall performance of the cement. A huge amount of water in the static reactor would reduce the carbonation depth due to water inhibition towards CO_2 diffusion.
- Adding 0.05 wt.% MWCNTs and 0.5 wt.% NGFs into the oil well cement would significantly improve the cement performance against the attack of CO_2.

Chapter 6: Conclusions and Recommendations

6.1. Conclusion

This dissertation attempted to develop a strategy and improve the performance of class G cement against the attack of CO_2 using nanomaterials, e.g. nano glass flakes (NGFs) and multiple-walled carbon nano tubes (MWCNTs). In a CO_2 storage site, carbonation of the neat cement takes place due to the interaction of the cement with dry/wet $scCO_2$, which is a self-healing process and initially enhance the compressive strength of the cement. However, due to the continuous diffusion of HCO_{3^-}, bi-carbonation of $CaCO_3$ causes a complete cement degradation. This degradation leads to an increase in porosity and permeability while reducing mechanical strength. Given the large surface area, significant physical, thermal and mechanical characteristics of nanomaterials, they could be a good option to improve the cement efficiency in a CCS site. The results obtained from integration of the cement with NGFs and MWCNTs, which were done, as part of this study, are summarized in the following sections.

6.1.1. Dispersed nanoparticles Vs Cement Performance

It is important to use a proper dispersion method and ensure that nanoparticles are uniformly distributed in the cement matrix. This would help to have a consistent rheology and good compressive strength. In this study, a sonication method was proposed to disperse NGFs and MWCNTs into the cement. It was observed that the sonicated samples with a certain amount of nanoparticles have a higher compressive strength, smoother microstructures and better rheology compared to the samples prepared by the conventional hand mixing approach. Although there have been some studies where adding surfactants has been proposed for a good dispersion of nanoparticles in the cement paste, in this study, to propose an effective but simple mixing approach, only sonication without any surfactant was suggested. It should be noted that if the dispersion parameters are changed, the amount of nanoparticles required for a good cement performance might be different.

6.1.2. Nanoparticles vs Cement Rheology

Rheology of the cement pastes changes with the amounts of nanoparticles added. Addition of NGFs gradually increases the viscosity of the cement pastes but keep the yield stress constant. On the other hand, a small amount of MWCNTs, say 0.025 to 0.05 wt.%, does not significantly change the viscosity while adding 0.075 to 0.25 wt.% may increase the viscosity by as much as 67%. Besides, the more MWCNTs is added into the cement, the higher the yield stress would be, which may affect the start-up pressure after a temporary shut-down and void filling properties of the cements (Clark et al., 1990). Hence, even though all the amount suggested for the cement replacement is acceptable based on the API free fluid tests, it is not recommended to add 0.25 wt.% MWCNTs to the cement as the high yield stress may cause difficulty during the cementing operation.

6.1.3. Nanoparticles vs Cement Microstructural

The results obtained from the TGA indicated that the nanoparticles may have a huge impact on the consumption rate of calcium hydroxide (CH). In fact, once a large amount of nanoparticles (1 wt.% NGFs and 0.1 wt.% MWCNTs) was added into the cement, the amount of CH increased, indicating that the nanomaterials could accelerate the cement hydration. X-ray diffraction (XRD) analysis also revealed that the nanoparticles could influence the cement strength. In addition, it appears from the SEM images that the nanomaterial can reduce the volume of micropores and microstructures, which reduce the cement porosity.

6.1.4. Nanoparticles vs Cement Strength

This study indicated that the nanoparticles can generally improve the compressive strength of the cement. It was observed that the sample with 0.5 wt.% NGFs would be the best cement in terms of the strength development. A long curing period can improve the cement strength. It was also noted that only a small quantity of nanoparticles is needed to enhance the compressive strength of the cement, given the fact that once the saturation threshold is exceeded, nanoparticles will not contribute into the strength development. The optimum quantity of NGFs and

MWCNTs to achieve a good compressive strength was then found as 0.5 wt.% and 0.05 wt.% respectively.

6.1.5. Carbonation of Nano-Modified Cement Composites

To do the carbonation test, a HPHT static reactor was used which could simulate a real CO_2 storage site condition. Changes induced in the physical and microstructure of the cement at this stage would be due to the formation of $CaCO_3$ as a result of interactions taking place between the cement and CO_2.

The result obtained from the carbonation test indicated that MWCNTs and NGFs based cements can provide a good performance in a CO_2 storage site. However, under a severe carbonation condition, MWCNTs works better than NGFs as it improves the cement strength, prolong the carbonation period and densifies the microstructure. Under a milder situation whereby the relative humidity is not favourable for CO_2 to diffuse into cement, all the cement samples experience a slower carbonation rate. A long carbonation period turns calcite into aragonite and reduce the compressive strength of the cement. Comparatively, MWCNTs would be a better option to resist against the carbonation. However, NGFs can be safely considered as an alternative option given that their good performance, in terms of lesser production of portlandite and relatively cheaper price.

6.1.6. Feasibility Analysis

The main reasons of considering NGFs and MWCNTs in this study was their salient characteristics under different pressure and temperature conditions. Given the fact that the prices of nanoparticles are relatively higher (NGFs costs $4.5 US per kg (China King Chemical) and MWCNTs costs $7.5-10 US per gram (Jiangsu XFNANO Materials), in this study, attempts were made to restrict the addition of these additives within 0.05 wt.% to 1 wt.%. In fact, to have an economically feasible cementing operation in a large scale, the concentration of nanoparticles in the cement should not go beyond 1 wt.%.

6.2. Recommendations

The aim of this research was to obtain a better understanding of the interaction mechanisms between the cement and nanoparticle and improve the performance of the cement in a CO_2 storage site. Due to the limitation of the static reactor equipment, carbonation period was only 56 days. Thus, the bicarbonation process did not take place. However, the interaction between CO_2, cement and nanoparticles were studied comprehensively and some results were presented based on the carbonation rate observed. It was concluded that the addition of nanoparticles (appropriate amount and well-dispersed) into the cement would improve the cement performance. There are rooms for the improvement/suggestions as below:

I. The test period should be prolonged to at least 6 months so that a better overview on the mechanism of carbonation process, especially the bicarbonation stage can be obtained.

II. Although optimum quantity used to improve the well cement was defined for both nanoparticles, it is suggested to use statistical methods or any other optimization tools to determine/validate the quantity of nanomaterials required for the best performance.

III. It is important to obtain a well-dispersed, stable nanoparticles solution before adding to the cement slurry. Hence, it is recommended to improve the ultrasonication approach so that the dispersion quality and stability of nanoparticles could be enhanced.

IV. Instead of using fresh water, saline water should be used as it can represent the real reservoir condition.

V. Mixing MWCNTs and NGFs together with cement could be considered in the future work. Both nanoparticles provide different kind of improvements in the cement structure. Hence, it is worth to investigate their combination once used in the cement exposed to CO_2.

VI. Last but not least, the effect of the cement additives such as retarder, dispersant and fluid loss agent should be evaluated on the nano-modified cement. This could help to learn more about the behaviour of the cement or any unfavourable properties that might be posed.

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Name: Dr Raoof Gholami ~~Mian Posteh~~

Position: Associate Professor

Date: 18th November 2019

Please return signed form to **michelle-tiong@postgrad.curtin.edu.my**

Appendix B

Permission from Dr Muhammad Ekhlasur:

Michelle Tiong <Michelle-tiong@postgrad.curtin.edu.my> Wed, Nov 20, 9:52 AM
to Muhammad

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Can Dr Muhammad sign and scan the document back to me? Regarding the copyright permission. They are needed so that I can complete my milestone 3 by this December.

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Position: Associate Professor

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Appendix C

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to Michelle

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